THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. L JULY 1955 No. 7

CONTENTS:

Report of the Standards and Specifications Committee - 332

Report of the Kaolin Committee - - - - - 333

Program of the Fourth Biennial Conference of the International Union of Leather Chemists Societies - 333

Pores in Collagen and Leather
By R. R. STROMBERG AND M. SWERDLOW - - - 336

Influence of Brining and Salt Curing on the Composition of Steer Hides *By* J. J. TANCOUS - - - - - 355

Abstracts - - - - - - - - - - - 366

SUBSCRIPTION: Members $12.00 a Year Non-Members $15.00

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

Entered as Second-Class Matter at Post Office, Easton, Pa.
Acceptance for Mailing at Special Rate of Postage as Provided for in Section 1103, Act of October 3, 1917, Authorized July 16, 1918

COPYRIGHT, 1955, THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Reliable Direct Sources the World Over

FOR

VEGETABLE TANNING MATERIALS

QUEBRACHO
WATTLE EXTRACT
WATTLE BARK
MANGROVE BARK
MYRABOLAMS & EXTRACT
VALONEA & EXTRACT
DIVI DIVI
CUTCH
SUMAC—LEAF & GROUND
TARA—PODS & POWDER
OAKWOOD EXTRACT, Swedish
LARCHBARK EXTRACT, Swedish

▼

U. S. of A. Sales Agents for "N.C.S." Brand South African Wattle Extract

U. S. of A. Sales Agents for "SENS" Brand Powdered Valonea Extract

The Olson Sales Agency

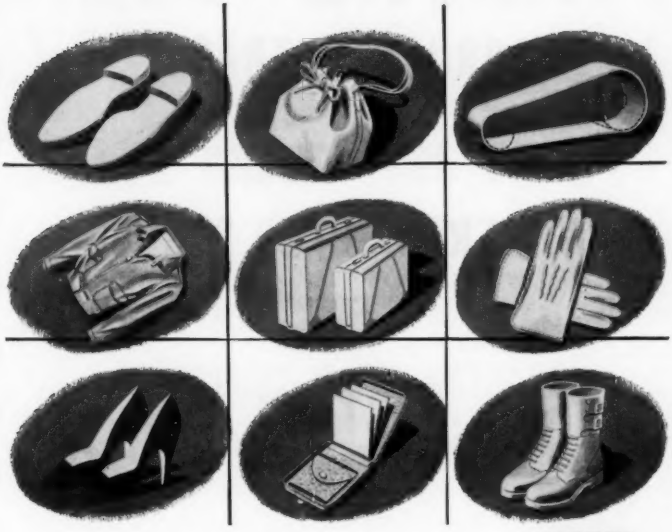
Import · Export

369 Lexington Avenue, New York 17, N. Y.

Coble Address:
"COROSAGE"

Telephones:
LExington 2-3733
2-3734
2-3735

No Matter What Kind of Leather You Make . . .



Gargoyle Leather Oils and Greases will help you make it better!

Name the kind of leather you make – sole or luggage, handbag or glove – you can improve its quality by using Gargoyle leather oils, greases and specialties!

In this famous family of tanning products you'll find the Sulfolines – exceptional fatliquoring agents . . . Curriers Greases – unsurpassed for leather stuffing . . . the Solenes, Sole Waterproofing Compounds and microcrystalline waxes . . . other leather oils and specialties – all made under the most exacting standards to assure peak quality.

Our products, technical facilities and 89 years' experience are always *at your service.* Call us *now.*

QUALITY AND SERVICE SINCE 1866

SOCONY MOBIL OIL CO., INC., TANNERS DIVISION, 26 BROADWAY, NEW YORK, N. Y.

GARGOYLE *LEATHER OILS and GREASES*

SPRUCE EXTRACT

POWDERED SUPER SPRUCE

LACTANX

■

Robeson Process Company

General Offices: 500 Fifth Avenue, New York, N. Y.

Operating Plant at Erie, Pa.

MECO EXTRACT

ONE GRADE—THE BEST

CHESTNUT WOOD EXTRACT

All Concentrations, Liquid to Dry Powder

Teas Extract Co.

6400 Centennial Boulevard

NASHVILLE 9, TENNESSEE

TENNESSEE PLANT
Nashville, Tenn.

ANDREWS PLANT
Andrews, N. C

Rohm & Haas Technical Help is Practical Help

All three of these men are working in a tannery; but only two are on the tannery payroll. The one in the middle is a Rohm & Haas technical representative. He spends most of his working hours in tanneries as a process counselor. He is supported by the experience and continuing research of the company's leather laboratories. As new knowledge is gained and new discoveries made, he translates them into practical results where they count, on the tannery floor.

For all steps in leather-making, from unhairing to finishing, Rohm & Haas provides not only the necessary products, but also technically-trained leather specialists who can help you to use these products to the best advantage.

Whatever your leather problems may be, it will pay you to talk them over with your Rohm & Haas representative.

SOME OUTSTANDING ROHM & HAAS LEATHER CHEMICALS ARE

OROPON—the pioneer enzyme bate, standard of the leather industry.

TAMOL—the dye assist that made pastel colors practical.

LEUKANOL—synthetic tan assist responsible for popular acceptance of white leather.

OROTAN—synthetic tanning material providing in itself a complete replacement for natural tannins.

PRIMAL—leather finishing materials in the form of aqueous dispersions of acrylic resins.

CHEMICALS FOR INDUSTRY

ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA 5, PA.

Representatives in principal foreign countries

OROPON, TAMOL, LEUKANOL, OROTAN *and* PRIMAL *are trade-marks, Reg. U.S. Pat. Off. and in principal foreign countries.*

MEAD CHESTNUT EXTRACT

is a superior tanning material, made by America's largest producer of vegetable tanning extracts

Repeated experience has shown:

A. Chestnut tanned leathers do not oxidize, darken on exposure to light, or develop an uneven color on aging, as do leathers tanned with many other materials, vegetable or synthetic.

B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

THE MEAD CORPORATION

Tannin Extract Division, Lynchburg, Virginia

LEDOGA S.p.A.

FOUNDED 1868

LEDOGA

Garressio-One of the 22 Italian plants controlled by Ledoga S.p.A.

WORLD'S LARGEST PRODUCERS OF

CHESTNUT EXTRACTS

Produced in *Italy*

Types: • Ledoga regular solid and spray-dried powdered Chestnut Extracts

• "Dulcotan", a sweetened Chestnut Extract

Properties: Highly Concentrated • Double Decolorized • Very Light Colored • Great Purity (due to very low non-tannin contents)

LEDOGA S.p.A. sells the total production of 22 of the 38 plants in Italy making Chestnut Extract.

*

Barkey

Importing Co., Inc.

44 East 53rd Street, New York 22, N. Y.

Exclusive Representative in the United States and Canada

VEGETABLE TANNERS

If you are interested in quality and customer satisfaction, you should investigate **ARKOTAN B.**

ARKOTAN B is a syntan that assists in the production of a smoother grain, improved tensile strength, fuller and rounder feel and a clear, even color.

ARKOTAN B assists in the solubility of your extracts, permitting greater penetration and better take-up and reduces the sludge in the bath when solid Quebracho is used.

ARKOTAN B when used in the color pit, wheel or tail liquors improves the appearance of the grain and maintains the correct acidity in the tail liquor without the addition of acid at this point.

ARKOTAN B is used extensively in the re-tan wheels to produce added weight. Excellent for use on chrome re-tan upper leather where a tight break and solid feel is required.

Samples or demonstration of **ARKOTAN B** are available upon request.

ARKANSAS COMPANY, Inc.
Newark, N. J.

Manufacturers of Industrial Chemicals for over 50 years

JACQUES WOLF CHEMICALS Produce High Grade Leather

SYNEKTAN 0-230
A liquid synthetic tannage that equals the qualities of vegetable extracts. Replaces Sumac. Used as a retan on chrome stock.

SYNEKTAN NPP
For high grade whites and pastel colors; produces full plump leather.

SYNEKTAN NCRP
Specialty syntan, used in combination with chrome tannage or in the dye bath for better grain.

TANASOL NCO
Syntan in beads, to use with extracts in the tanning and retanning operations.

TANASOL PW
Syntan in beads, to use with NCO for bleaching chrome stock and in retanning chrome stock. In the dye bath for good level colors.

FUNGIZYME BATES
Pancreatic bating salts of standard, controlled quality.

BATE A & AS For sheep skins and sole leather.

BATE B & BS For furniture leather, side leather and calf skins.

BATE C & CS For goat skins.

SULPHONATED OILS (Various Bases)

MONOPOLE OIL (For Finishing)

EMULSIFIERS AND DETERGENTS (For Good Degreasing)

Samples and information upon request.

JACQUES WOLF & CO.
Chemicals PASSAIC, N.J.

Plants in: **Clifton, N.J., Carlstadt, N.J., Los Angeles, Calif.**

DIAMOND A COMPOUND

TESTED and proved for 40 years—Diamond A is recognized as the Tanners' standard sponging and washing compound.

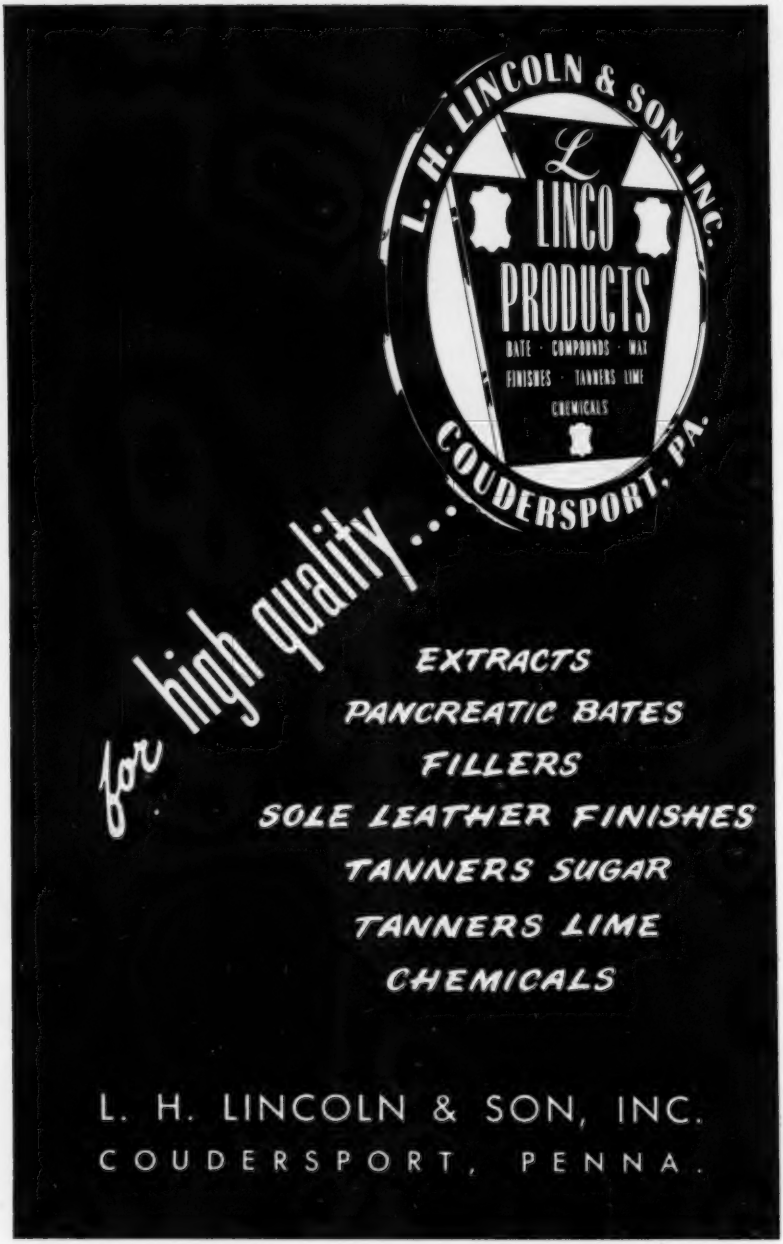
Here's why. Diamond A does a *double* job — (1) It prepares sole leather for rolling and protects the grain. (2) Used as a dip after rolling, it toughens the grain and improves color and finish.

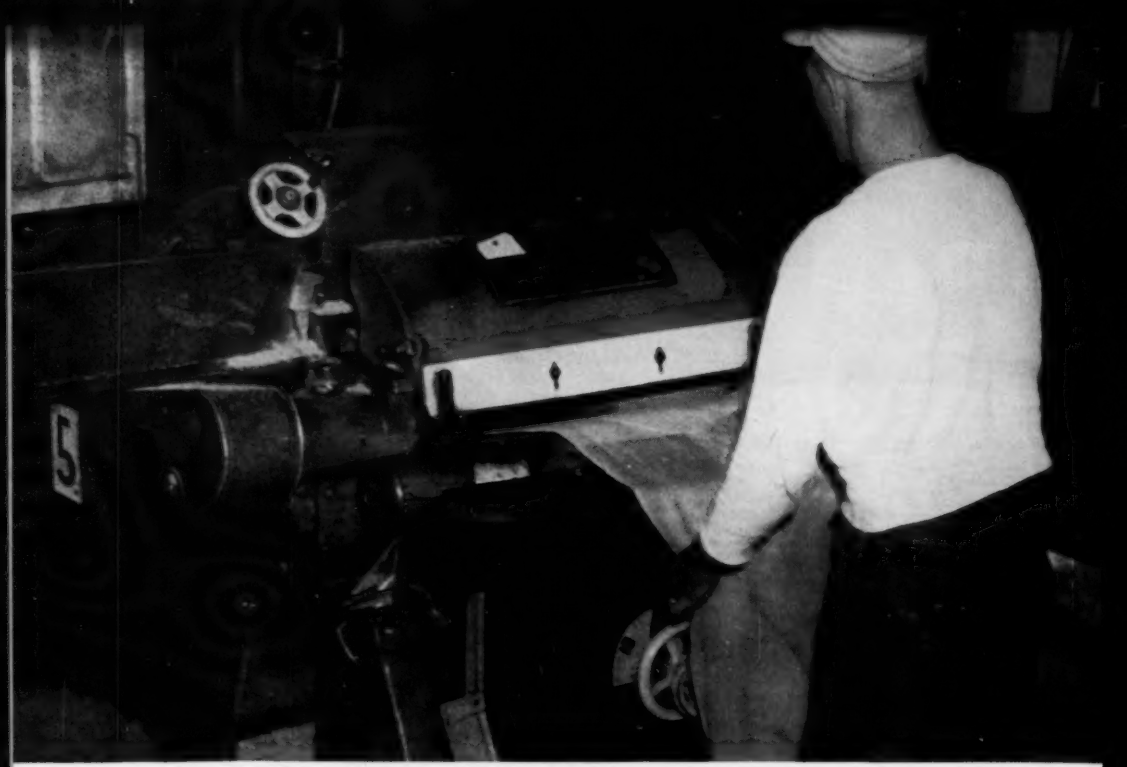
Why delay? Let the Borne, Scrymser representative give you full particulars on Diamond A. You'll agree it's in a class by itself.

OTHER BORNE, SCRYMSER SPECIALTIES
(Get the Facts about These, Too!)
P **COMPOUND for WHEELING**
A **COMPOUND for SPONGING**
Supreme A Compound
Bretolene • Saxon Oil

BORNE SCRYMSER Since 1874
Our Laboratory Facilities are always at your disposal

BORNE, SCRYMSER COMPANY Elizabeth, N. J. Charlotte, N. C.


L. H. LINCOLN & SON, INC.
LINCO
PRODUCTS
BATE · COMPOUNDS · WAX
FINISHES · TANNERS LIME
CHEMICALS
COUDERSPORT, PA.
for high quality . . .
EXTRACTS
PANCREATIC BATES
FILLERS
SOLE LEATHER FINISHES
TANNERS SUGAR
TANNERS LIME
CHEMICALS
L. H. LINCOLN & SON, INC.
COUDERSPORT, PENNA.



Shaving leather at Northwestern Leather Company, Sault Ste. Marie, Michigan.

How TANAK® MRX lets you hold... or even better shaver's weight

Once it permeates your stock, TANAK MRX Tanning Agent builds larger molecules by polymerization, making your leather plumper and more round. You can hold or even better shaver's weight from the pasting plates. The result is improved bellies and flanks, tighter break, tighter grain and better temper.

Tanners everywhere are discovering the market-building advantages of TANAK MRX and, working closely with Cyanamid's Technical Staff, are upgrading both their white and their colored stock.

To realize the benefits of TANAK MRX, contact your Cyanamid representative. To help solve your product and process problems, the complete staff and facilities of Cyanamid's modern application laboratory are at your disposal... along with our full selection of leather processing chemicals.

To make leather better through chemistry...

Begin at the beginning to make good leather—that's what tanners do when they use DEPILIN® Unhairing Agent. It gives you cleaner, whiter stock and better process control.

AMERICAN Cyanamid COMPANY

LEATHER CHEMICALS DEPARTMENT

30 Rockefeller Plaza, New York 20, N. Y.

In Canada: North American Cyanamid Limited, Toronto & Montreal

To prevent SPOILAGE

USE.. BSM-11 or BUTROL

as part of Good housekeeping practice

BSM-11 is highly effective in controlling the growth of microorganisms which digest hide substance during processing. BSM-11 is a liquid, thus easily added to the systems directly from the drums.

It has been demonstrated in many tanneries that the synergistic combination of bactericides and fungicides in BSM-11 provides efficient, economical control of bacteria, molds and yeasts which damage skins and hides.

Our representative will give technical assistance on the most effective use of BSM-11 in your process.

BUCKMAN LABORATORIES, INC.

Manufacturing Chemists • Memphis 8, Tennessee • Representatives in Most Countries

MICROORGANISM CONTROL SPECIALISTS

Lucky for Leather there's Nitrex!

FOR NITREX GIVES LEATHER A HOST OF WONDERFUL NEW COMPETITIVE SELLING PROPERTIES!

New toughness! With its own high film strength, this specially developed latex greatly strengthens leather against scuffing and all sorts of abrasion.

New life! Nitrex® protects leather against water, gasoline, oil stains—against alcohols, glycols, paint and ink driers, lacquer solvents. It keeps it soft and supple—resistant to sunlight and aging—free of crazing and cracking for years of service.

New beauty! Nitrex provides tack-free finishes—transparent or opaque—in a wide variety of deep, lasting colors.

New ease of treatment! A water dispersion, Nitrex is highly compatible with casein and other leather finishing materials.

Treat *your* leather products to Nitrex. See why more and more leather finishers are turning to this special acrylonitrile latex for the beauty and toughness they need in a highly competitive market. For more information on the use and many advantages of Nitrex, write to Naugatuck—world's leader in the development and supply of latex compounds.

Naugatuck Chemical

Division of United States Rubber Company
Naugatuck, Connecticut

US RUBBER

BRANCHES: Akron • Boston • Charlotte • Chicago • Los Angeles • Memphis • New York • Philadelphia • IN CANADA: Naugatuck Chemicals, Elmira, Ont. • Rubber Chemicals • Synthetic Rubber • Plastics • Agricultural Chemicals • Reclaimed Rubber • Latices • Cable Address: Rubexport, N. Y.

EXTRACTS & RAW TANNING MATERIALS

QUEBRACHO

solid:
CF del C CROWN REALTAN

liquid:
SM . . . SMS

ground or spray dried
ORDINARY . . . PUREX

WATTLE

solid:
KENMOSA ELEPHANT

liquid:
WATEX

ground or spray dried
WATTLE

MYRABOLAM

spray powdered & solid

CHESTNUT

spray powdered & solid

MANGROVE & WATTLE BARK
WHOLE & CRUSHED MYRABOLAMS
VALONEA TARA SUMAC DIVI DIVI
SPRAY POWDERED MANGROVE & VALONEA

Importers and Processors

THE RIVER PLATE CORPORATION
Executive Offices: CHRYSLER BUILDING, NEW YORK 17, N. Y.

TANNIN EXTRACT DIVISION
Sales Office & Plant: 573-589 FERRY ST., NEWARK 5, N. J.

Subsidiary: THE TANNIN CORPORATION of MASS. Office & Plant: Peabody, Mass.

THE WATTLE CROP HAS UNIFORMITY AND ASSURANCE OF SUPPLY

TANNERS know what it means to get uniformity of color and purity in extracts. Wattle Extract has such extra appeal because the bark is plantation-grown as a crop.

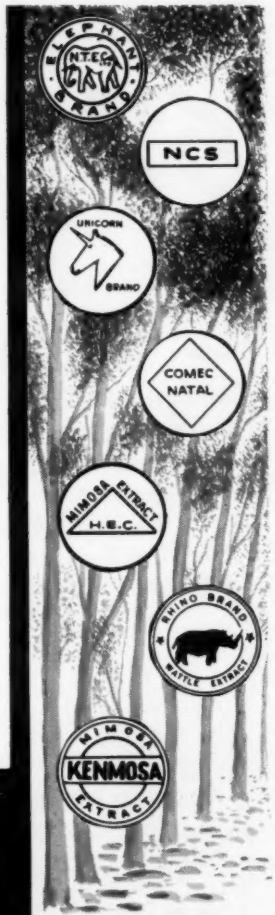
Specially selected trees are planted and given all the care that modern forestation methods make possible. This means quality regularity as regards color and purity.

Wattle trees are cut and bark-stripped when they have grown from 7 to 9 years, depending upon locality, thereby insuring future continuity of supply.

The other attractions of Wattle Extract . . . its rapid penetration, affinity for hide, versatility . . . are too well known to the tanning industry to need emphasis.

The supply of WATTLE will not run out, and remember,

WATTLE MAKES GOOD LEATHER



South African Wattle Extract Mfrs. Asso.
Pietermaritzburg, Natal, Union of South Africa

Kenya Wattle Manufacturers Association
Nairobi, Kenya, East Africa

AT YOUR SERVICE . . .

Let our

67 years of specialized experience work for you . . . profitably

ATLAS

Guaranteed **OILS**

- **NEATSFOOT OILS**
- **SULPHONATED COD OILS**
- **SULPHONATED NEATSFOOT OILS**
- **SPLIT OILS**
- **MOELLONS, and many specialty Products**

ATLAS REFINERY SINCE 1887 QUALITY LEATHER OILS NEWARK, N.J.

A Name and Symbol
Pre-eminent in the Tannery Industry

● For over half a century, ATLAS has been a leader in the production of Quality Oils for the Tanning Industry, through extensive research to serve you better. ATLAS specialized research, plus many years of practical experience in the production of consistently high-quality, guaranteed oils is your assurance of uniformity to meet definite specifications. Give your leathers the "quality look" with ATLAS Oils.

ATLAS *Refinery, Inc.*

142 LOCKWOOD ST. NEWARK 5, N. J.

QUEBRACHO EXTRACTS

"SUPREMO"
BRAND
SOLID-ORDINARY

"LUNA"
BRAND
COLD WATER SOLUBLE

INTERNATIONAL PRODUCTS CORPORATION

29 BROADWAY, NEW YORK 6, N. Y.

The Only American Manufacturer of Quebracho In South America

FACTORY AT PUERTO PINASCO, PARAGUAY

MANUFACTURERS:
LIQUID QUEBRACHO EXTRACTS
•
FACTORY:
Staten Island, N. Y.

IMPORTERS:
MYRABOLAMS
WATTLE BARK
DIVI-DIVI
VALONIA
ETC.

Representatives:

Harvey J. Boutin & Son
San Francisco, Calif.

Yocum Faust, Limited
London, Canada

Gonzalez, Ramirez y Cia
Havana, Cuba

The R. J. Vogel Company
Mexico City, Mexico

BARKEY

Importing Co. Inc.

44 EAST 53rd STREET • NEW YORK 22, N. Y.

IMPORTERS

VEGETABLE TANNING EXTRACTS AND RAW MATERIALS

- Wattle Bark
- Wattle Extract
- Quebracho Extract
- Mangrove Bark
- Valonia Cups, Beards
- Divi divi
- Valonia Extract, Valex Brand
- Sicily Sumac
- Myrabolans

SOLE AGENTS FOR UNITED STATES & CANADA

for

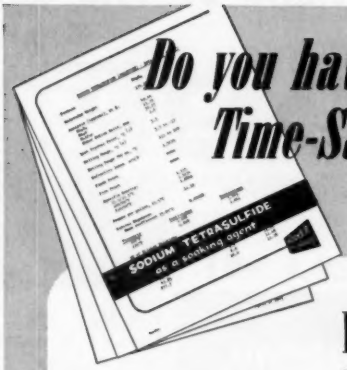
ITALIAN CHESTNUT EXTRACTS

SOLID & POWDERED

Produced by

LEDOGA S. p. A.

MILANO, ITALY



Do you have this Time-Saving Data on Soaking?

TANNERS REPORT SAVINGS UP TO THREE DAYS

Skins soaked only 24 hours in water at 65° to 70° F., containing 0.7% Hooker Sodium Tetrasulfide, are sufficiently softened for drumming.

Even flint dried steer hides are frequently ready to process after only 48 hours in the same strength solution.

A 24-hour soak for green salted hides and skins, in 0.3% Hooker Sodium Tetrasulfide solution, gives cleaner hides, more uniform tannin distribution, a higher leather yield.

HOOKER BULLETIN 505 tells how tanners are cutting soaking time in half by using Hooker Sodium Tetrasulfide solution. It describes uses and advantages of this time-saving and money-saving new chemical. A request on your company letterhead will bring you a copy.

The Hooker technical staff, constantly at work on processing needs of the leather industry, is always on call for help in solving your particular problems.

HOOKER ELECTROCHEMICAL COMPANY

3 UNION ST. - NIAGARA FALLS, N. Y.
CHICAGO, ILL. - NEW YORK, N. Y.
LOS ANGELES, CALIF. - TACOMA, WASH.

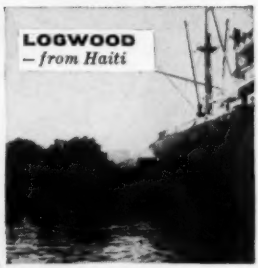
CAUSTIC SODA • MURIATIC ACID
PARADICHLOROBENZENE • CHLORINE
SODIUM TETRASULFIDE • SODIUM SULFIDE

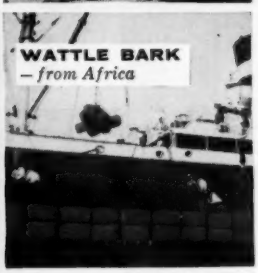
HOOKER CHEMICALS ®

10-1396

FROM THE FAR CORNERS OF THE GLOBE

A few photos of some of the loading and unloading operations at the J. S. YOUNG CO. pier in Baltimore. J. S. Young Company's own railroad encircles the entire plant.

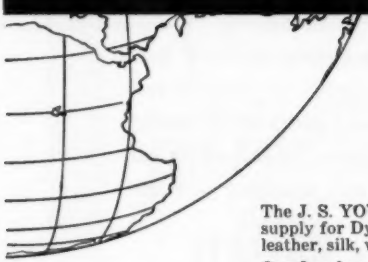




THE
J. S. Young Company
SINCE 1869

– known everywhere as
ONE OF AMERICA'S FOREMOST AND
RELIABLE PROCESSORS AND IMPORTERS OF

Tanning Extracts



The J. S. YOUNG CO., since 1869, has been the dependable source of supply for Dye Woods for all branches of industry . . . dye woods for leather, silk, wool and synthetic textiles.

Our firm has the reputation, over all these years, for prompt delivery direct from our Baltimore or our warehouses in Peabody, Mass. . . . shipments in any quantity – from barrel to tank car.

LOGWOOD • WATTLE BARK • SUMAC • DIVI-DIVI • GAMBIER
QUEBRACHO • MYRABOLAM • OSAGE ORANGE
CHESTNUT WOOD EXTRACT • FUSTIC • HYPERNIC • TANNIC ACID

We also manufacture the famous CHEMBARK *natural tanning extracts for the Chemtan Co.*

The J. S. YOUNG CO.

2701-2733 BOSTON ST. BALTIMORE 24, MD.

Branches: PHILADELPHIA • MILWAUKEE • NEW YORK • DANVERS, MASS.

CHEMBARK

The Leading
Vegetable Retan Extracts
for Chrome Tanned Leathers

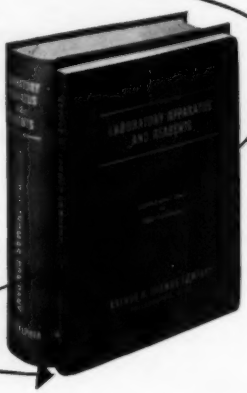
Roundness
Fullness
Cutting value

CHEMTAN COMPANY
CHEMTAN
PORT WASHINGTON, N.Y.

DEVELOPMENT AND INTRODUCTION OF
BETTER **CHEM**ICALS FOR **TAN**NING

Now being distributed . . .

SUPPLEMENT
to the
THOMAS CATALOGUE



1600 New Items
Current Price List

NOW . . . 22,000 items offered to you for immediate shipment from our stock.

This new Supplement follows the tradition of the Thomas catalogue on which the following comment was made by a leading scientific periodical:

"More than a catalogue . . . a source of reference the user will place on his shelves with manuals and textbooks."

The encyclopedic catalogue of 1472 pages and the new 264-page supplement list a total of approximately 22,000 current items, adequate stocks of which are carried for immediate shipment.

The selection of apparatus is based upon more than half a century of experience in supplying the needs of laboratories of Chemistry and Biology, both large and small. Choice was made after careful consideration, and testing by the Thomas technological staff. Items included are therefore offered with assurance of being satisfactory for the purpose intended.

This new Supplement with current Price List, in combination with the general catalogue, constitutes an up-to-date listing of one of the most comprehensive assortments of apparatus and reagents available from any single source.

SUPPLEMENT

Detailed and factual listings, fully indexed, of new items added to our stock since 1950.

Complete "Price List" of current apparatus items in *both* catalogue and supplement.

Supplement now being mailed to all who have the Thomas catalogue.

SYMBOL OF QUALITY
A.H.T.CO.
SPECIFICATION
LABORATORY APPARATUS

ARTHUR H. THOMAS COMPANY

Laboratory Apparatus and Reagents

WEST WASHINGTON SQUARE PHILADELPHIA 5, PA.

Teletype Services: Western Union WUX and Bell System PH-72

JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. L JULY 1955 No. 7

DEAN WILLIAMS ---------- *Editor*

EDITORIAL BOARD

H. B. MERRILL R. B. HOBBS F. O'FLAHERTY
R. E. PORTER J. H. HIGHBERGER H. G. TURLEY

Only such correspondence as pertains to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Correspondence in reference to subscriptions, advertising and other business should be addressed to the Secretary, Dept. of Leather Research, University of Cincinnati, Cincinnati 21, Ohio.

Checks for subscriptions and advertisements should be made payable to the American Leather Chemists Association.

Subscriptions—Members, $12.00 annually; Non-members, $15.00 annually.

Published monthly by the American Leather Chemists Association.

Entered as Second-class Matter at the Post Office at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

Copyright 1955, by the American Leather Chemists Association.

PAST PRESIDENTS OF THE A. L. C. A.

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VETCH, W. K. ALSOP, L. E. LEVI, C. R. OBERFELL, R. W. GRIFFITH, C. C. SMOOT, III, J. S. ROGERS, LLOYD BALDERSTON, J. A. WILSON, R. W. FREY, G. D. MCLAUGHLIN, FRED O'FLAHERTY, A. C. ORTHMANN, H. B. MERRILL, V. J. MLEJNEK, J. H. HIGHBERGER, DEAN WILLIAMS, T. F. OBERLANDER, A. H. WINHEIM, R. M. KOPPENHOEFER, H. G. TURLEY.

OFFICERS 1954-'55

President—E. S. Flinn, Ardslea, Route 8
Chillicothe, Ohio

President-Elect—E. B. Thorstensen, S. B. Foot Tanning Company, Red Wing, Minnesota.

Secretary-Treasurer—Fred O'Flaherty, Department of Leather Research, University of Cincinnati, Cincinnati, Ohio.

Council

Mieth Maeser, United Shoe Machinery Corporation, Research Division, Balch Street, Beverly, Massachusetts.

Dominic Meo, Jr., Salem Oil and Grease Company, Salem, Massachusetts.

E. D. Compton, Eagle-Ottawa Leather Co., Grand Haven, Mich.

Robert Stubbings, Div. of Leather Technology, Lehigh University, Bethlehem, Pa.

Robert G. Weldon, Seton Leather Co.,
Newark 4, N. J.

REPORT OF THE STANDARDS AND SPECIFICATIONS COMMITTEE

During the period May 1954 - May 1955, the following Proposed Revisions of Federal Leather Specifications have been presented to the Committee for comments and approval:

KK-L-00167a, Chamois, Revision No. 2.
KK-L-311a, Method 2211, Resistance to Grain Cracking.
KK-L-311a, Methods 1011, 1111, 1121, 1211, Sampling.
KK-L-311a, Methods 6211, 6221, Moisture Determination.
KK-L-271c, Strap Leather.
KK-L-170, Amendment No. 1, Goatskin, Chrome Tanned.
KK-W-231a, Welting.
KK-L-00181c, Hydraulic Packing, Vegetable Tanned.
KK-L-00177c, Hydraulic Packing, Mineral Tanned.
KK-L-00201c, Lace Leather.
KK-B-00201c, Belting, Flat, Vegetable Tanned.
KK-L-00171d, Harness, Vegetable Tanned.
KK-L-00169a, Horsehide.
KK-L-00291d, Upholstery.
KK-L-00261d, Sole Leather, Sampling on Area versus Weight Basis.

Sampling of Cut Stock to avoid "edge effect" in conjunction with KK-L-191, Insoles, and MIL-11636b, Insoles.

In most instances the Proposed Revisions were approved by the Committee with only minor changes recommended. In judging Specifications KK-L-00177c, Hydraulic Packing, Mineral Tanned, the assistance of the manufacturers of this item was sought and suggestions made for changes in specification limits.

Action on KK-L-00261d and Methods 6211, 6221, of KK-L-311a is pending at the time of the annual meeting.

CARL G. TELANDER, *Chairman,*
A.L.C.A. Standards and Specifications Committee

REPORT OF THE KAOLIN COMMITTEE

May 16, 1955

The Committee has examined the sample of Kaolin, batch B-9498, recently submitted by the Arthur H. Thomas Company, and finds it to comply with the Official Specifications. The Committee has therefore approved this batch for use.

Respectfully submitted,

I. D. CLARKE
F. F. MARSHALL
G. W. SCHULTZ
G. W. STANBERY
G. V. DOWNING
A. N. KAY, *Chairman*

LECTURES AND PAPERS TO BE PRESENTED AT THE FOURTH BIENNIAL CONFERENCE OF THE INTERNATIONAL UNION OF LEATHER CHEMISTS' SOCIETIES IN STOCKHOLM, AUGUST 1st - 4th, 1955

MONDAY, AUGUST 1st

10:00 a. m. Official Opening of Conference.

10:20–10:50 Presidential Address: "A Swedish Pioneer of Leather Technology in the Berzelain Epoch".

10:50–12:00 Noon—*The Max Bergmann Memorial Lecture* on "Our Present Knowledge of Collagen", by DR. WO. GRASSMANN (in German).

Presiding: MR. J. R. BLOCKEY

Symposium on "The Properties of Leather"

1:00 p.m.–1:10 p.m.—Introduction by the Symposium Chairman: MR. J. R. BLOCKEY.

1:10–2:00 R. G. MITTON: "The Physical Properties of Leather".

2:15–3:00 J. R. KANAGY: "The Properties of Leather: Their Measurements and the Establishing of Standards".

3:15–4:00 E. BAUMANN: "Some Aspects of Properties of Leather from the Shoe Manufacturing Point of View".

4:20–4:50 P. CHAMBARD: "The French Experience with Quality Control of Leather for Consumer's Goods" (in French).

5:00–5:20 E. SIMONCINI: "Special Properties of Leather, which are not yet well known".

5:20–6:00 Discussion.

TUESDAY, AUGUST 2nd

Symposium on "The Fundamentals of the Chemistry of Tanning Process"

9:00 a.m.–9:10 a.m. —Introduction by the Symposium Chairman: DR. K. H. GUSTAVSON.

9:10–9:40 K. G. A. PANKHURST: "The Contribution of the Study of Monolayers of Proteins to the Problem of Tannage".

9:50–10:30 D. BALANYI: "The Chrome Tanning Process" (in German).

10:30–10:50 Discussion opened by DR. E. MITCHELL.

10:50–11:40 T. WHITE: "The Vegetable Tannage".

11:40–12:00 Discussion opened by MR. N. L. HOLMES, who will stress the issue of the modern sole leather tannage.

1:30 p.m.–2:15 p.m.—A. KUNTZEL: "The Fundamentals of Tanning with Synthetic Tannins including the Resin Tannage" (in German).

2:15–2:30 Discussion opened by DR. C. GASTELLU.

2:30–3:15 G. OTTO: "The Interaction of Skin with Aromatic Tanning Agents, Dyestuffs and Auxiliaries" (in German).

3:30–4:15 H. G. TURLEY: "The Correlation of the Processes in Leather Manufacture".

4:15–5:00 Discussion. Concluding resumé by DR. D. BURTON.

WEDNESDAY, AUGUST 3rd

Presiding: DR. H. G. TURLEY

9:00 a.m.–9:20 a.m.–B. M. DAS and S. N. BOSE: "Determination of Amino Acids of Collagen of an Indian Buffalo Hide."

9:30–9:50 J. R. KANAGY: "Studies of Leather by Means of a Sonic Technique".

10:00–10:20 N. L. HOLMES and H. G. WOLLENBERG: "Tanning as a Rate Process". (presented by DR. H. G. WOLLENBERG).

10:30–10:50 R. G. MITTON: "The Diffusion of Water-Vapor in Leather".

11:00–11:15 P. J. VAN VLIMMEREN: "The Use of Hide Powder for Evaluating the Tannin Balance in Vegetable Tanning".

11:25–11:40 Y. SAKIMOTO: "On the Preferential Tannin Absorption by Hide Powder from Blended Vegetable Tan Liquor".

11:50–12:10 Y. NAYUDAMMA and D. RAMASWAMY: "Non-aqueous Titration Technique—I. A method for the determination of salt contents in vegetable tan liquors". (presented by B. M. DAS).

12:15–12:30 A. LARSSON: "On the Reaction of Polyvinylpyrrolidone (PVP) with Vegetable Tannins".

12:35–12:50 C. G. TELANDER: "Some Observations on the Tannage of Sole Leather".

THURSDAY, AUGUST 4th

Presiding: DR. A. ENGELER

9:00 a.m.–9:15 a.m. W. PENSE: "On Synthetic Leather Oils" (in German).

9:20–9:35 R. BOSE: "Some Points in Manufacturing Combination Tanned Leather" (in German).

9:45–10:00 F. STATHER: "The Resistance of Leather against Proteolytic Degradation" (in German).

10:10–10:25 P. PEUREUX: "Special Chestnut Extracts" (in French).

10:30–10:45 C. ALABOUVETTE and C. ROUANET: "The Dyeing of Suede Leather" (in French).

11:00–11:20 P. CHAMBARD: "The use of Synthetic Resins in Sole Leather Manufacture" (in French).

11:30–11:50 W. WEBER: "The Examination of the Fastness Properties of Leather Dyestuffs" (in German).

Presiding: DR. WO. GRASSMANN

1:30 p.m.–1:45 p.m. J. A. SAGOSCHEN: "Newer Instruments for Measuring the Color of Leather" (in German).

1:55–2:35 H. SCHOLZ: "The Problem of Sewage in the Leather Industry" (in German).

2:35–3:15 Discussion.
Presiding: DR. K. H. GUSTAVSON

3:15–5:00 Open Meeting of Conference to receive reports from Commissions. General Meeting. Venue of next Conference. Closing of Conference.

Pores In Collagen and Leather*

By ROBERT R. STROMBERG and MAX SWERDLOW

National Bureau of Standards
Washington, D. C.

ABSTRACT

The approximate magnitude and location of pores in collagen are demonstrated. The pore-size range from 100 to 20,000 Å in radius was investigated by a mercury pressure porosimeter method. Pore-size distribution curves of a number of leathers and collagenous tissues indicated that a significant pore volume was associated with pores less than 1000 Å in radius. Electron micrographs of collagen fibrils obtained from mercury-impregnated kangaroo tail tendon showed periodic arrangements of opaque areas that were interpreted as pore sites of about 150 Å in radius within single fibrils. A helical configuration of subfibrillar elements is suggested by the geometry of swollen collagen fibrils as well as of mercury-impregnated fibrils. The size and distribution of the pores in the fibrous structure of leather is considered in relation to such processes as tanning, water vapor transmission, and impregnation of leather with polymers.

I. INTRODUCTION

Significant advances in understanding the mechanisms involved in the processes of leather technology can be made through investigations of the fundamental structure and properties of collagen [1], [2]. Many of the unique properties of leather are believed to stem from certain inherent structural characteristics of the fibrous network that is formed in nature. From considerations of such properties as density, porosity, and texture, it would appear that there is a considerable void volume. A knowledge of the distribution of pores, their size, shape, and location, would be of direct interest to the leather chemist and technologist in understanding the behavior of

*Presented at the Fiftieth Annual Meeting of the American Leather Chemists' Association, Bedford, Pennsylvania, on June 7, 1954.

leather. Physical data on the pore structure within the matrix would provide additional understanding of such properties as water vapor transmission and resistance to flexural fatigue [3]. Such processes as tanning and the impregnation of leather with other polymers [4] are considered to be dependent in a large measure upon the porous structure.

This paper is concerned with the size distribution of pores in the structural matrix of collagen and leather. Of equal interest is the geometry of the collagen fibril insofar as it relates to pores within the structure of the individual fibrils.

2. Material and Methods

Among the materials investigated by the porosimeter method were a group of vegetable-tanned leathers, raw hide, and air-dried kangaroo tail tendon, listed in the following table. Specimens B, C, and D were all obtained from a small

Materials Investigated

Specimen	Material	Thickness	"Dry" weight
		cm.	g.
A	Vegetable-tanned finished sole leather	0.572	3.226
B	Degreased vegetable-tanned crust leather, grain split	0.069	0.956
C	Degreased vegetable-tanned crust leather, corium split	0.089	3.154
D	Degreased vegetable-tanned crust leather, flesh split	0.056	1.922
E	Corium split of raw hide, dehydrated by solvent exchange process	0.160	1.722
F	Corium split of raw hide, dehydrated by solvent exchange process, rewetted and evaporated	0.147	6.720
G	Air-dried kangaroo tail tendon	——	17.436

area of a central location of one bend of vegetable-tanned crust leather. Only the first grain and flesh splits and the center of the corium were used. The degreasing was accomplished by extraction with chloroform in a Soxhlet extraction apparatus. Specimen E was prepared by dehydrating the wet cowhide by a solvent exchange process. The wet skin was immersed in acetone, split, immersed in alcohol, and finally reimmersed in acetone and the acetone allowed to evaporate at room temperature and atmospheric conditions. Only the center portion of the corium was used. Specimen F was prepared by rewetting an adjoining portion of the hide used for specimen E and soaking it in water for a few hours. This rewet skin was then allowed to dry at room temperature. Specimen G consisted of air-dried bundles of tendon obtained from kangaroo tail.

Thickness measurements were made with a standard deadweight gage [5]. The "dry" weight in grams is given for each specimen. This value was ob-

tained after drying overnight in a forced-air oven maintained at 80°C. It was necessary to vary the size and weight of the specimen used in order to match the void volume of the specimen with the capacity of the dilatometer used for the porosimeter measurements.

Two separate methods were employed in this study. A pressure porosimeter method [6] was used to obtain pore-size distributions in the range of 100 to 20,000 Å in pore radius and the methods of electron microscopy were employed to elucidate the magnitude and location of pores within the individual collagen fibrils [7].

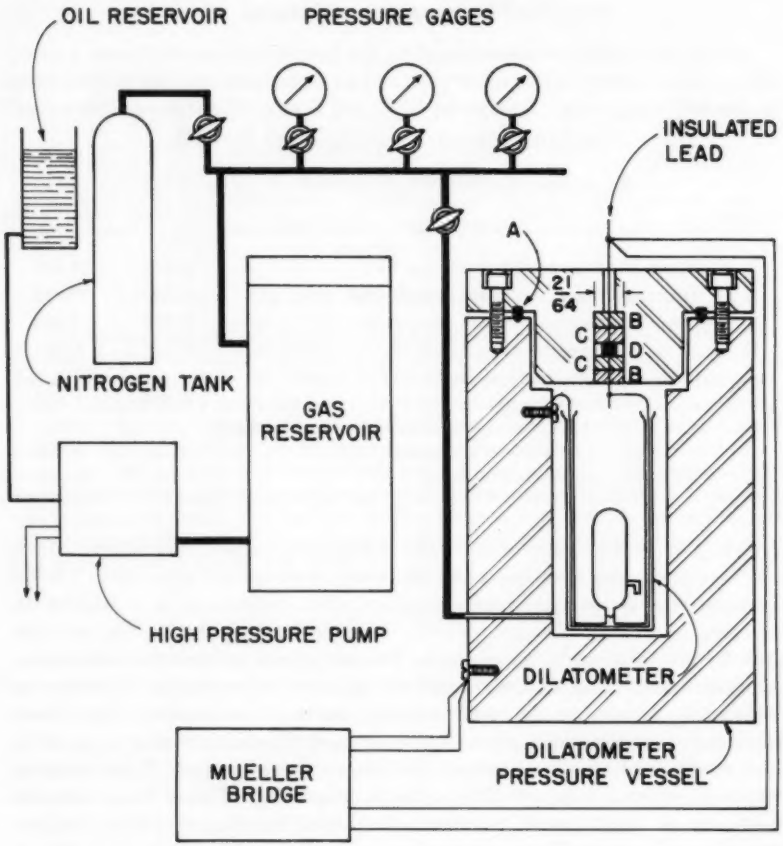


FIGURE 1.—Schematic view of the pressure porosimeter apparatus.
A—Copper washer
B—Bakelite washers
C—Rubber washer (GR-M)
D—Tool steel silver-soldered to wire.

Figure 1 is a schematic view of the pressure porosimeter apparatus. Essentially, the method is based on the theory that specified pressures are required to force a nonwetting liquid (mercury) into pores of certain radii. The pertinent relationship is:

$$Pr = -2\ \sigma \cos\ \theta \tag{1}$$

where P is the pressure, r is the pore radius, σ is the surface tension of the liquid, and θ is the contact angle between the liquid and solid. A cylindrical shape, having a circular cross section, is assumed for each pore. Constancy of surface tension and contact angle also are assumed. For a given value of r there will be a corresponding value of P leading to a characteristic pressure-volume curve. Ritter and Drake [8] developed the porosimeter method based on this relationship. Their method involved forcing a measured quantity of mercury under a known pressure into a previously prepared porous specimen. In addition, they defined an expression for the pore-size distribution:

$$D(r) = \frac{P}{r}\frac{dV}{dP} \tag{2}$$

where $D(r)$ is the distribution function and dV is the difference between the initial and final volumes for the pressure range dP. The values of dV/dP were obtained from the pressure curve by the method of secants. The distribution function $D(r)$ is not a number distribution. It has the dimensions of area and when the $D(r)$ vs. radius curve is integrated between any two limits the pore volume within that range may be obtained. By the porosimeter method a pore-size distribution curve is obtained which is characterisitic of a given pore population in any material.

The methods of electron microscopy were applied to the kangaroo tail tendon because this material was considered to be similar to other mammalian collagen and was known to yield an easily recognized microstructure. Bulk pieces of air-dried kangaroo tail tendon were evacuated to a pressure of about 10^{-5} mm. of Hg, immersed in mercury, and subjected to hydrostatic pressures as high as 10,800 psi. Following this, the tendon was removed from the pressure vessel, cut into smaller pieces, and beaten in clean tap water in an electric food blender for 10 minutes in order to separate individual fibrils of of collagen. The temperature of the water never exceeded 35°C. Other specimens of the air-dried tendon were not subjected to the mercury treatment but were dispersed in the blender in the above manner. Specimens were prepared by pipetting drops of the dispersed material onto collodion-covered screens. These were allowed to dry in room air (approximately 22°C. and 50 per cent relative humidity). To create a three-dimensional aspect and provide additional contrast, some specimens were shadowed with about 20 Å of palladium at an angle such that the shadow length would be about

four times the altitude of the specimen. Micrographs of the shadowed specimens have been reproduced as negative prints. The RCA Type EMU-50 kv electron microscope was used.

3. Results and Discussion

3.1 *Porosimetric Measurements*

A typical pressure-volume curve relating the cumulative volume of mercury forced into the pores, V, to the absolute pressure, P is shown in figure 2. Time intervals of about one hour were necessary to establish a steady state at each of the pressures used. For the flesh split of degreased vegetable-tanned crust leather the curve (figure 2) obtained upon decreasing the pressure from 10,550 to 49 psi. did not coincide with the increasing pressure curve. The difference between the starting and end points indicates that 0.217 ml. of mercury per gram of leather was retained by the specimen. This corresponded to approximately 40 per cent of the pore volume explored in the range from 100 to 18,000 Å in pore radius. This hysteresis effect occurred with all the specimens studied, but the percentage of mercury retained varied with the material.

Curves have been selected that illustrate the nature of the pore-size distribution in the range from approximately 100 to 20,000 Å in radius, for the type of material studied here. Figure 3 illustrates the distribution as a function of pore radius for vegetable-tanned finished sole leather. Figure 4 shows the distribution as a function of pore radius for the grain, corium, and flesh splits of degreased vegetable-tanned crust leather. Figure 5 represents the distribution as a function of pore radius for kangaroo tail tendon. From a known distribution the total amount or percentage of void volume can be determined for selected ranges of pore sizes. For example, the distribution curve (figure 4) for specimen D, the flesh split of vegetable-tanned crust leather, shows that of the void volume represented by pores in the range investigated (250 to 18,000 Å in radius) approximately 14 per cent was associated with pores ranging from 250 to 1000 Å in radius, and approximately 5 per cent with pores ranging from 250 to 500 Å in radius. In another case, the distribution curve (figure 5) for specimen G, kangaroo tail tendon, shows that of the void volume represented by pores in the range investigated (100 to 18,000 Å in radius) approximately 75 per cent could be assigned to pores ranging from 100 to 1000 Å in radius and approximately 50 per cent to pores ranging from 100 to 350 Å in radius.

In evaluating the results obtained by the pressure porosimeter method, certain sources of error must be kept in mind. The assumption of the circular cross-sectional area used in equation (1) is an approximation of the true shape. It is also assumed in these calculations that the contact angle and surface tension are not pressure dependent and that unknown contaminations

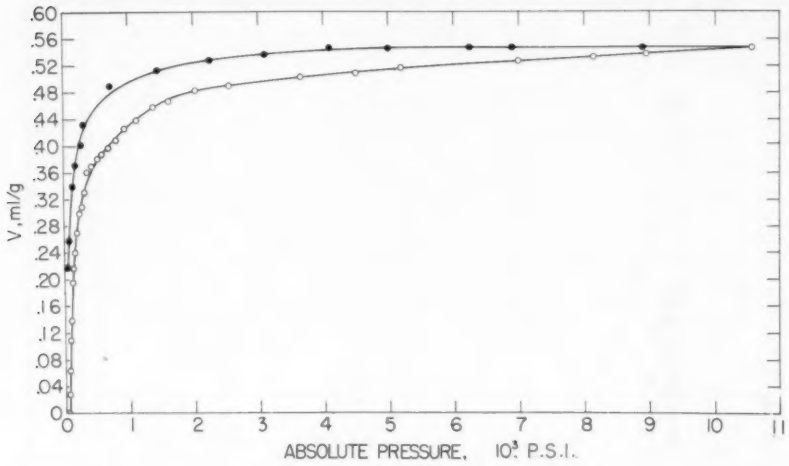


FIGURE 2.—Increasing and decreasing pressure curves for flesh split of degreased vegetable-tanned crust leather, Specimen D.
○—Increasing pressure ●—Decreasing pressure

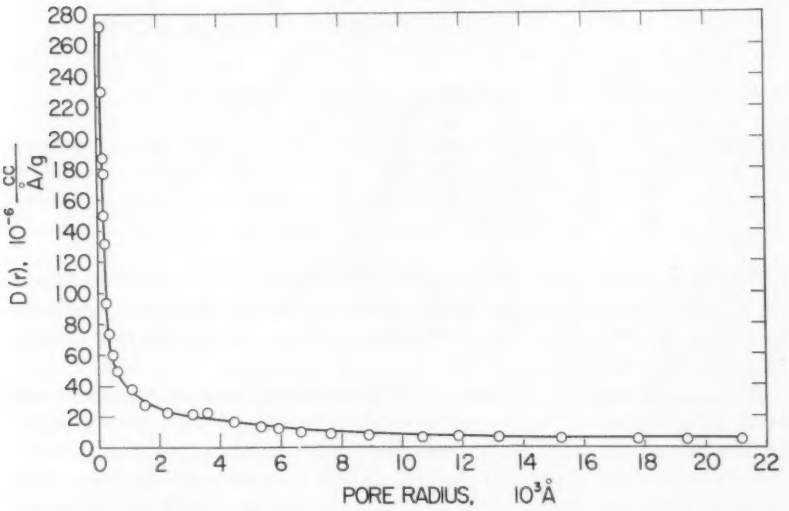


FIGURE 3.—Pore-size distribution curve for vegetable-tanned finished sole leather, specimen A. The distribution function, D(r), in cubic centimeters per angstrom per gram is plotted against pore radius, r, in angstroms.

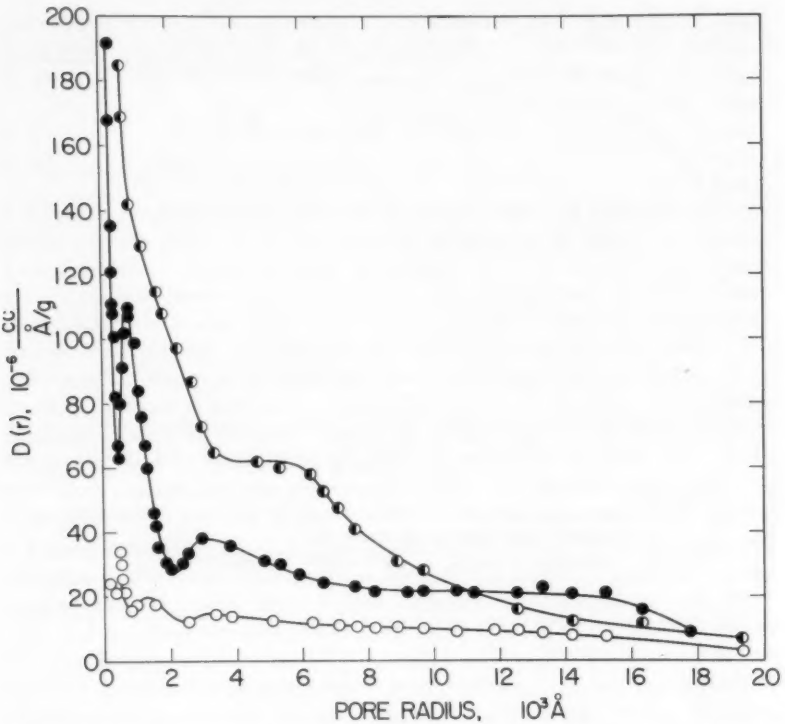


FIGURE 4.—Pore-size distribution curve for grain, corium, and flesh splits of degreased vegetable-tanned crust leathers.
◐—Grain split, specimen B.
○—Corium split, specimen C.
●—Flesh split, specimen D.

will not alter these values. Although absolute determinations might be affected, it seems reasonable to expect that these assumptions would not appreciably affect the validity of intercomparisons among materials having similar structure and treatment.

A statistical analysis applied to the distribution curves[6] indicated that small irregularities in the curves were probably due to experimental error and smooth curves should be drawn. There were, however, peaks along some of the curves which appeared to be real. These were more directly associated with the particular specimen studied and were not necessarily typical of the material in general. Duplicate specimens showed a coincidence of distributions, except for the peaks. In general, the curves can be regarded as representative of the pore-size distribution of the types of materials studied.

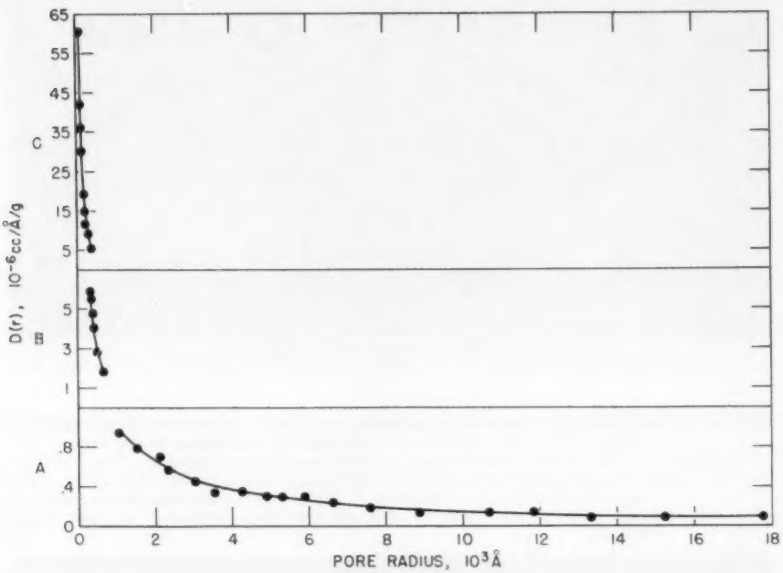


FIGURE 5.—Pore-size distribution curve for kangaroo tail tendon, specimen G. Part A represents the pore-size distribution from 1000 to 18,000 Å; part B, from 350 to 800 Å; and part C, from 100 to 400 Å.

Large variations may be observed among the curves shown in figure 4 for the three splits of vegetable crust leather. Over the greater part of the range measured, the grain split (specimen B) contained the largest volume of pores of all sizes; whereas, the corium split (specimen C) contained the smallest total volume. From the statistical analysis cited above, it is uncertain whether the flat portion of the distribution curve of grain split crust leather that occurred in the region of 5000 Å pore radius is real. In the regions of the maxima and minima in the distribution curve of the flesh split (specimen D), the shape of the curve in the vicinity of the minimum at 500 Å and the maximum at 1000 Å, respectively, appears to be real. The "dip" in the curve at about 2500 Å may not be real. The sharp fall in the curve for the flesh and grain split specimens in the region of the very small pore radii appears to be real.

It has been shown [6] that the corium split of raw hide dehydrated by a solvent exchange process (specimen E) and the corium split of raw hide dehydrated by evaporation of water content at room temperature (specimen F) gave distribution curves similar to that obtained for finished sole leather (figure 3). This similarity arises from the large contribution of the corium to the pore volume. The two specimens of raw hide were different in physical

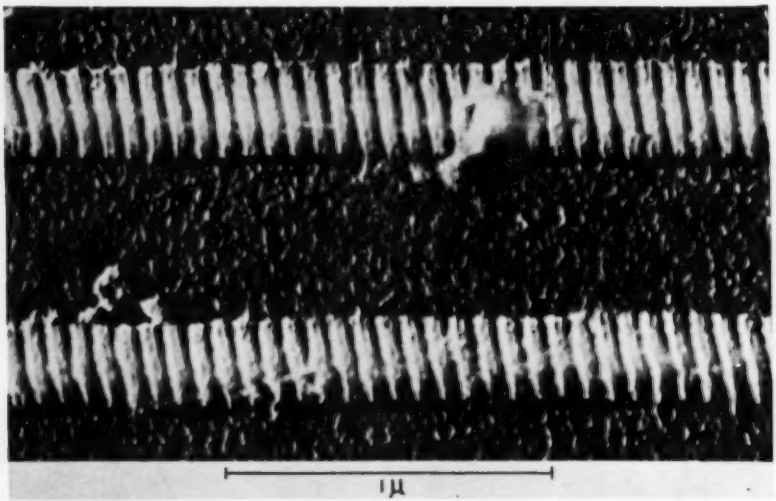


FIGURE 6.—*Electron micrograph of a palladium shadowed specimen of two individual collagen fibrils obtained from a water dispersion of kangaroo tail tendon.*

A typical characteristic periodic structure is shown. The striations indicate a right-handed helical formation with a helix angle of 9°. This angle lies between the element of the helix and the perpendicular to the helix axis. This axis is common with the fibril axis (horizontal in these micrographs).

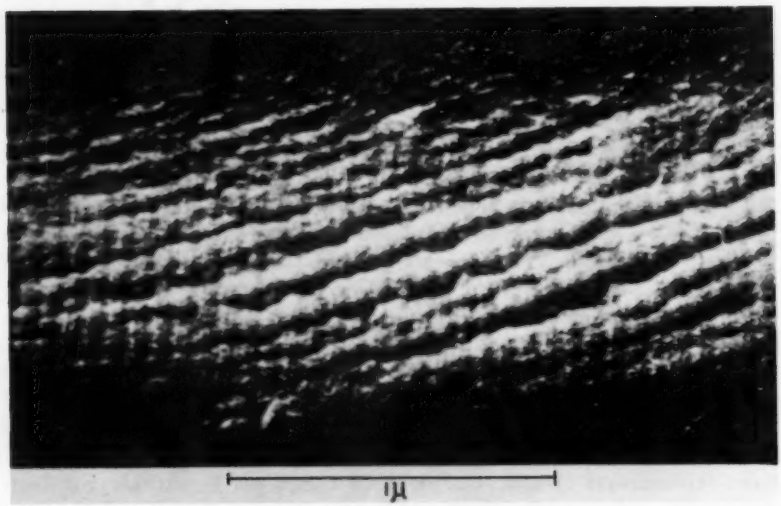


FIGURE 7.—*Electron micrograph of a single, swollen, palladium shadowed collagen fibril obtained from a water dispersion of kangaroo tail tendon.*

Remnants of the characteristic periodic structure seen in figure 6 may be observed. The *single* fibril shown here has been altered so that the transverse dimension (vertical in these micrographs) is approximately four times that seen in figure 6. The geometric discontinuities in the opened, flattened structure are assumed to be the sites of pores within the fibril. The subfibrillar elements make a left-handed helical configuration with a helix angle of about 72°.

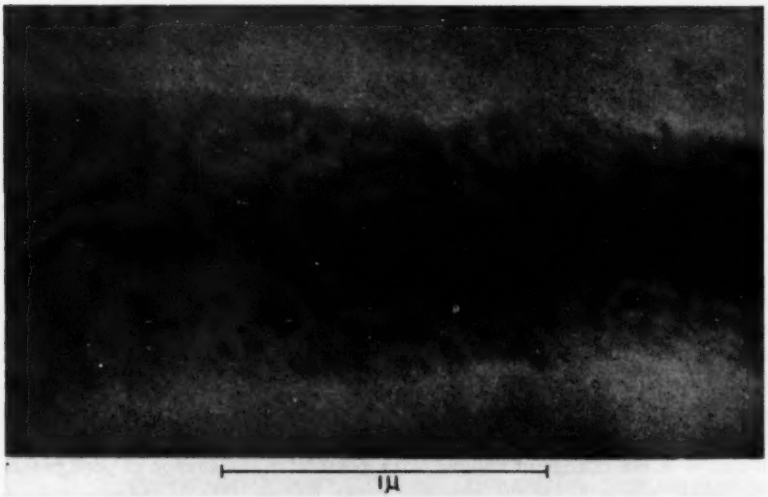


FIGURE 8.—*Electron micrograph of a single, swollen, unshadowed collagen fibril obtained from a water dispersion of kangaroo tail tendon.*

An opened, disrupted structure is shown with a helical configuration of subfibrillar elements. The opaque individual spots are viewed as incidental debris.

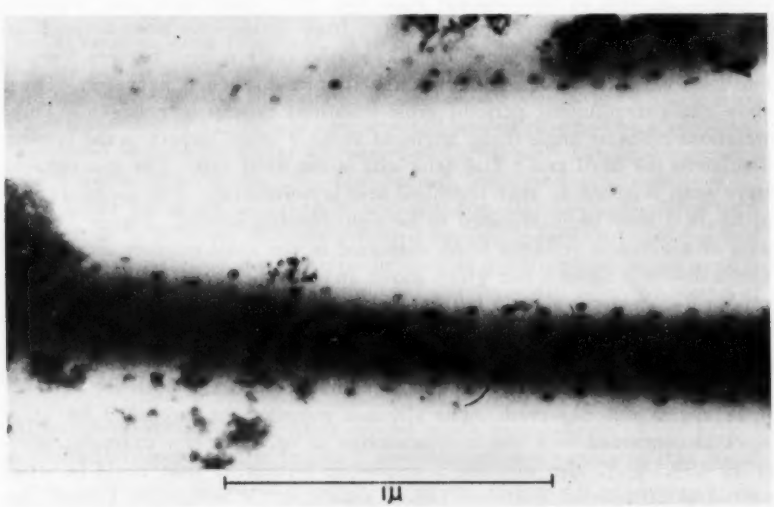


FIGURE 9.—*Electron micrograph of unshadowed, mercury-impregnated collagen fibrils obtained from a water dispersion of kangaroo tail tendon.*

The dense elliptically-shaped areas, approximately 250 Å by 350 Å, are arranged periodically within the fibrils. If parallel lines were ruled across the fibril axis connecting these spots in the lower fibril, one set of lines would be approximately 1000 Å apart with a helix angle of about 9°; another set would be approximately 750 Å apart with a helix angle of about 72°. It is presumed that the denser areas resulted from the presence of mercury or a compound of mercury entrapped in these intrafibrillar pores.

appearance. Specimen E was soft and pliable and specimen F was hard and inflexible. The distribution curve for specimen E fell above and approximately parallel to that of specimen F. This displacement indicates that the solvent exchange process produced a more opened structure.

All the collagenous tissues studies thus far showed a sharp rise in the distribution curve in the region of 100 Å. There existed, therefore, a significant void volume concentrated in pores of small radii. Furthermore, this volume must be comprised of an extremely large number of small-sized pores. The distribution curve obtained for kangaroo tail tendon showed a close similarity to the curves representing finished sole leather, the corium splits of crust leather, and raw hide. Figure 5 shows that for the pore-size range 1000 to 18,000 Å the change in volume with respect to the change in pore radius was small; whereas, for the pore-size range 100 to 1000 Å, the pore volume sharply increased inversely with respect to pore radius.

3.2 *Electron Microscopy*

To provide additional evidence of the existence of pores in leather and collagen as well as information regarding their magnitude and location, figures 6, 7, 8, and 9 have been selected from an electron microscopical investigation of fibrils* obtained from kangaroo tail tendon. Figures 6 shows two individual collagen fibrils obtained from a dispersion in water. These show the characteristic periodic cross-striations typical of collagen. These striations make an angle (helix angle) of about 9° with respect to the perpendicular to the fibril axis. The helix axis is the fibril axis. The micrographs have been oriented so that the fibril axis is horizontal. The configurations in figure 6 may be interpreted to be right-handed helices. Figure 7 shows part of a different collagen fibril, dispersed in the same manner as were the fibrils shown in figure 6 but which shows an opened, flattened structure. The subfibrillar elements show a left-handed helical configuration. The elements in this case make a helix angle of about 72°. No special significance can be given to helix direction inasmuch as an approximately equal number of occurrences of left-handedness and right-handedness for both 9° and 72° helix angles was observed. The electron micrographs published by other workers concerned with the microstructure of collagen, (for example: references [9, 10, 11, 12]), also indicate a geometric formation that could be interpreted as an opened, flattened helical structure. Whether the helical configuration observed in the electron micrographs was a result of specimen preparation or was a manifestation of the much smaller inherent helical

*The terminology generally used throughout the literature has been adopted for this paper. The large aggregates at the limit of resolution of the unaided eye and seen with the aid of the light microscope are termed *fibers*. Smaller components still visible in the light microscope are called *primitive fibers*. These are composed of *fibrils*, which require the electron microscope for adequate resolution. the smallest filamentous structures presently resolved with the electron microscope have been termed *filaments*. The *subfibrillar structures* referred to in this paper have dimensions larger than that of a filament and smaller than that of a fibril.

configuration currently proposed for the collagen molecule [13, 14, 15, 16] is uncertain.

Even though the fibril seen in figure 7 was given the same treatment as those seen in figure 6, it appears that the former was swollen during the ten-minute dispersion of the kangaroo tail tendon in water. Upon drying, such a swollen fibril could have collapsed and flattened into the disrupted, opened form observed. The transverse dimension of the fibril seen in figure 7 is about four times larger than that of an unopened fibril such as those seen in figure 6. The physical structure of the subfibrillar matrix observed in figure 7 suggests, therefore, that geometric discontinuities exist *within* the fibril; these discontinuities are assumed to be the sites of pores within the matrix. Because the expanded subfibrillar matrix probably was distorted, only an approximation of the shape and size of such pores is possible. However, the position of pore sites that might have existed in the original undisrupted fibril is indicated.

Examination of the mercury-impregnated collagen fibrils provided additional information about the arrangement of these small pores within the fibril. The effect of mercury impregnation is shown by a comparison of figures 8 and 9. Figure 8 is representative of a single, unshadowed collagen fibril that was not treated with mercury. The incidental particles of debris associated with the preparation are randomly distributed. Although the effect is not as clear as when shadowed, as in figure 7, the opened structure shows the same helical configuration of subfibrillar elements. On the other hand, figure 9 is representative of a single, unshadowed collagen fibril taken from a water dispersion of a bundle of kangaroo tail tendon that had been previously subjected to mercury under a pressure of 10,800 psi. The fibril appeared to be differentially "stained." The opened, disrupted structure seen in figures 7 and 8 was not observed in any of the specimens impregnated with mercury. It is believed that the mercury became lodged in the pores and retarded the penetration of water into the fibrillar structure and, consequently, the swelling of the fibril. It is presumed that mercury or a compound of mercury make up the spots of denser material. Receptive areas of the collagen fibril might selectively adsorb or combine with mercury, as with other heavy metals. These spots are distributed in a more or less periodic fashion*

Although no direct comparisons can be made, examination of the helical subfibrillar structure seen in figures 7 and 8 indicates a geometry that could

*Since completion of this manuscript, in a private communication, Professor F. O. Schmitt, of the Massachusetts Institute of Technology, reported some X-ray diffraction data obtained from samples of dry and moist kangaroo tail tendon that had been immersed in mercury under a pressure of 10,800 psi. The data, which had been kindly obtained by Dr. R. E. Dreikorn of the United Shoe Machinery Corporation, were as follows: "The large-angle pattern was fairly typical of collagen although the 2.86 Å meridional arc seemed unusually intense. The side-chain spacing of 10.55 Å in the dry preparation increased to 11.6 Å at 50 per cent humidity and 11.9 Å at 75 per cent humidity. Thus, although the mercury impregnation may limit the side chain swelling, the treated material seems more reactive to water than if it had been well tanned. The small angle diffraction pattern appeared to be fairly similar to that of normal tendon; the 3rd, 6th, 9th, and 16th orders were accentuated.

"I have occasionally seen structures, somewhat like those which you interpret as being mercury-filled pores, in skin fibrils stained with PTA. Whether they represent open spaces in the protofibrillar lattice is not known."

account for many pore sites across and along the subfibrillar elements. The number of spots in a given row across the fibril seen in figure 9 is considerably less than the number of such possible pore sites. This may be accounted for in two ways. Many of the pore sites seen in figures 7 and 8 are probably considerably smaller in radius than 100 Å in the unopened state. Within the limits of the apparatus and procedure described here, the maximum pressures that could be obtained would force mercury into cylindrical pores no smaller than 100 Å in radius. It is expected that some of the mercury might be dislodged when the pressure was released and also in the subsequent treatment during specimen preparation. When parallel lines were ruled across the fibril axis connecting these spots in figure 9 (lower fibril), one set was about 1000 Å apart with a helix angle of about 9°. The characteristic cross-striations observed in collagen, figure 6, also showed this same helix angle but the periodic spacing was about 750 Å. Another set of lines following a helical path around the fibril axis was about 750 Å apart with a helix angle of about 72°. This is the same value obtained for the helix angle in the case of the opened fibrils. The individual spots have an elliptical shape. These are approximately 250 Å in one dimension and 350 Å in another, the longer dimension being parallel to the fibril axis. For a comparison with the circular cross section of the pore assumed for calculating the distribution curve, these dimensions would approximate a pore radius of the order of 150 Å. It would appear then that these micrographs provide a visual experimental confirmation of the approximate magnitude and location of pores in collagen fibrils independently deduced from theoretical considerations of distributions obtained from porosimetric measurements.

4. Technological Considerations

From a technological viewpoint these findings regarding the size and distribution of pores in the fibrous network of collagenous tissue can be used to speculate concerning the physical properties of leather.

As a first approximation the pores can be divided into groups corresponding to the structure of the fibrous tissue. The group of largest pores exists between fibers and probably, for the most part, consists of pores larger than 20,000 Å in radius. This group is not included in this study. The remaining void volume is made up of pores existing between primitive fibers, between fibrils, and within fibrils. Although the pore-size distribution can probably be divided into the groups indicated above, it must be remembered that overlapping undoubtedly occurs. It is entirely conceivable that dimensions usually regarded as falling in the inter-fibril group exist also in some instances between fibers.

In general, the porosity should depend not only upon the inherent structure of the material but also upon the previous history and tanning process. It

may be expected that in the case of the larger pores, associated with inter-fiber distances and with inter-primitive-fiber distances, there would be a large dependence upon the inherent weave and intertwining of the collagenous tissue and the previous treatment given the specimen. For different specimens obtained from the same hide location and given the same processing, different distributions in the range of large pore radii would, therefore reflect differences in the inherent structure. In the case of the smaller pores associated with the interfibril distances, there would probably be a much smaller dependence upon source and treatment.

The distribution curves indicate that the range covered by the inter-primitive-fiber distances extends upwards from a minimum of approximately 1000 A in pore radius. The pores of smaller radii may be assigned to the interfibril and intrafibril distances. It can be observed that all the curves tend to coincide at pore radii smaller than 1000 Å. This is especially evident in the range less than 500 Å, where the curves more nearly approach each other as the radius decreases. Some of this coincidence might be attributed to the decrease in the sensitivity of the method for the small pore-size range. However, from the statistical analysis of the curves [6] it appears that the similarity of the curves is primarily attributable to the similarity of the inherent fine structure of the various materials studied. Additional studies at higher pressures are necessary to investigate the portion of the curve corresponding to radii less than 100 Å. It might be anticipated that only small differences in this range will exist for specimens obtained from the same animal species.

The wide displacement of the distribution curves for the three splits observed in figure 4, all obtained from the same source of vegetable-tanned crust leather, may be taken to demonstrate the differences in the natural structure of each split. Comparison of the distribution curves of specimen E, the corium split of raw hide prepared by a solvent exchange process, with specimen C, the corium split of tanned crust leather, shows very little difference. This would indicate that the tanning process may not appreciably change the distribution of pore radii in the range from 500 to 20,000 Å, and that the size distribution may be fairly constant for the types of treatment received.

Mechanisms for the transmission of water vapor through leather have been discussed by Kanagy and Vickers [17]. In addition to the generally accepted concept of the porous structure of the fibrous network, it would appear from the study reported here that consideration should be given to the significant void volume associated with pores of the order of 150 Å in radius within the individual fibril. These pores should be regarded as additional paths for the transmission of water vapor. Furthermore, the profound changes that occur in the physical properties of leather when penetrated by water might be explained by the penetration through pores within individual fibrils that are

more closely associated with the molecular structure of collagen than the larger void spaces occurring outside the fibrils. Moreover, the existence of a porous structure among the subfibrillar elements of collagenous materials furnishes additional information to the findings of Rougvie and Bear[18] on the changes in the intrafibrillar structure occurring with swelling.

The impregnation of leather with various polymers[4] has raised some interesting questions about the mechanism involved. Although the chemical interaction of leather and the impregnant is another very important aspect of the problem, the geometrical factors of the process can be studied from considerations of the physical structures involved. For example, with a knowledge of the pore-size distribution of a given leather and a knowledge of the shape and size of the particles of the impregnating polymer[19], the leather technologist could estimate the quantity of material that might enter the pore structure, provided that the leather and impregnant were compatible. Measurements made on the amounts of polyisobutylene in impregnated leather, with and without the grain side present[20], confirm the observation made from figure 4 that the grain split contains the greatest volume of pores of all sizes. With basic information about the physical structure of the leather and the impregnant, the technologist would be in a better position to control the extent of impregnation and thereby control the properties of the finished product.

Acknowledgment

The authors are pleased to acknowledge the helpful suggestions of Jerome Gross of the Harvard Medical School and Massachusetts General Hospital, and the stimulating discussions with Charles E. Weir, Everett L. Wallace, and Joseph R. Kanagy of the National Bureau of Standards.

References

1. J. H. Highberger, A half century of progress in collagen chemistry, *J. Am. Leather Chemists' Assoc.* **48,** 704-719 (1953).
2. W. Grassman, Electron optical and chemical studies on the structure of collagen, pp. 195–212, The chemical structure of proteins (A ciba foundation symposium, J. and A. Churchill Ltd., London, England, 1953).
3. T. J. Carter and J. R. Kanagy, A flex tension test for leather, *J. Am. Leather Chemists' Assoc.* **49,** 23-42 (1954).
4. R. Oehler, S. Dahl, and T. J. Kilduff, Treatment of leather with polyisobutylene, *J. Am. Leather Chemists' Assoc.* **47,** 642-60 (1952).
5. Federal Specification KK-L-311a, Leather; Methods of Sampling and Testing, Method 1021, (General Services Administration, Business Service Center, Washington 25, D. C., January 19, 1953).
6. R. R. Stromberg, Pore-size distribution in collagen and leather by the porosimeter method, *J. Research NBS* **54,** 73-81 (1955) RP2567.
7. M. Swerdlow and R. R. Stromberg, Collagen pores determined by electron microscopy, *J. Research NBS* **54,** 83-90 (1955) RP 2568.

8. H. L. Ritter and L. C. Drake, Pore-size distribution in porous materials. I. Pressure porosimeter and determination of complete macropore-size distributions. *Ind. Eng. Chem. Anal. Ed.* **17,** 782-6 (1945).
9. J. T. Randall, Editor, Nature and structure of collagen, p. 235 (Academic Press, Inc., New York, N. Y., 1953).
10. F. O. Schmitt and J. Gross, Further progress in the electron microscopy of collagen, *J. Am. Leather Chemists' Assoc.* **43,** 658-75 (1948).
11. G. C. Nutting and R. Borasky, Electron microscopy of collagen, *J. Am. Leather Chemists' Assoc.* **43,** 96-110 (1948).
12. R. W. G. Wyckoff, Electron Microscopy Technique and Applications, pp. 203-4 (Interscience Publishers, Inc., New York, N. Y., 1949).
13. L. Pauling and R. B. Corey, The structure of fibrous proteins of the collagen-gelatin group, *Proc. Nat. Acad. Sci.* **37,** 272-81 (1951); see also; A discussion on the structure of proteins, *Proc. Roy. Soc.* (London B) **141,** 1-97 (1953).
14. R. S. Bear, The structure of collagen fibrils, pp. 69-160 in "Advances in Protein Chemistry," Vol. VII (Academic Press, Inc., New York, N. Y., 1952).
15. C. Cohen and R. S. Bear, Helical polypeptide chain configuration in collagen, *J. Am. Chem. Soc.* **75,** 2783-4 (1953).
16. F. H. C. Crick, A structure for collagen, *J. Chem. Phys.* **22,** 347 (1954).
17. J. R. Kanagy and R. A. Vickers III, Factors affecting the water vapor permeability of leather, *J. Research NBS* **44,** 347-62 (1950) RP 2082; *J. Am. Leather Chemists' Assoc.* **45,** 211-42 (1950).
18. M. A. Rougvie and R. S. Bear, An X-ray diffraction investigation of swelling by collagen, *J. Am. Leather Chemists' Assoc.* **48,** 735-51 (1953).
19. R. R Stromberg, M. Swerdlow, and J. Mandel, Electron microscopy of synthetic elastomer latices, *J. Research NBS* **50,** 299-309 (1953) RP2419.
20. R. Oehler, Leather Section, National Bureau of Standards, Washington 25, D. C., private communication.

Received April 9, 1955

Discussion

M. Maeser (United Shoe Machinery Corporation):

I am probably as poor a man as there is in the Association to discuss a paper of this kind. I know nothing about electronic microscopes or the ways in which results are obtained by their use. But maybe we can get somebody else that knows more about it than I do to discuss your paper.

To start things out, Dr. Stromberg, I see a couple of things I would like ask questions about.

Somwhere in your last four slides you show the mercury distribution in the pores. How certain do you feel that the mercury which is shown in the slides is actually penetrating the fibril?

R. R. Stromberg: If we could have the last slide, please: (Last slide shown on screen—See Fig. 9.)

The electron optically opaque areas observed as spots in the micrograph of the individual collagen fibril shown here are believed to be mercury or a compound of mercury. If the mercury penetrated diametrically through the

fibril, the electron micrograph would exhibit a dark zone completely across the fibril. The spots are interpreted as indicating preferential penetration in localized areas.

It is possible that greater penetration occurred while the fibril was exposed to mercury under hydrostatic presures as high as 10,800 psi. and that some of the mercury that could have entered at such pressures might have been freed when the pressures were reduced to normal. In addition, in the preparation of the specimen for electron microscopy, it is possible that some of the mercury might have been shaken loose from the pores in the fibril when the mercury impregnated bulk pieces of kangaroo tail tendon were beaten in water.

The fact that in the electron micrograph we can observe various degrees of opaqueness of the spots and varying degrees of sharpness of the boundaries of the spots could be interpreted as an indication of various levels of penetration and would result in the differential scattering of the electron beam as observed in the recorded image.

MAESER: There is another aspect of the same problem. Is it possible that the mercury, in addition to being forced into the fibrils, has formed a superficial or measurable coating around the outside of the fibrils, giving you a false indication of the amount of pore volume which actually exists.

STROMBERG: May I please have supplementary slide "B": This is a preparation that has been impregnated with mercury and shadowed with about 20 Å of palladium at such an angle that a projection in the surface would cast a shadow about four times its altitude. If a layer of mercury completely surrounded the surface of the collagen fibril it would appear dark and probably opaque in the electron micrograph. If the coating of mercury was incomplete, discontinuities in the surface would show up with good contrast. Note the three dimensional nature of the spheroidal masses seen in the background. These are believed to be colloidal mercury and show up quite distinctly as a result of the shadowcasting technique.

MAESER: Is there anyone in the audience who would like to ask questions?

JOHN H. HIGHBERGER: (United Shoe Machinery Corporation): Did I understand you to say that the distance between these rows is about 1,000 angstrom units?

STROMBERG: Yes.

HIGHBERGER: Do you think that is any connection between that and the size of the regular collagen periods?

STROMBERG: We would have been happier if there were a simple arithmetic relationship between the characteristic 640 Å unit axial periodicity, but we

have no explanation for this discrepancy. It is possible that some structural distortion took place somewhere in the course of the experiment.

A. N. KAY (Howes Leather Company, Inc.): Dr. Stromberg, in the last regular slide that you showed, (See Fig. 9) the spots seemed to be in groups of four transverse to the fibril axis. It appeared, just visually, as if two were opposite each other and the other two also opposite each other, the four's looking as if they were two ducts mutually at right angles with a blob of mercury at each end.

STROMBERG: I had not observed that and I do not know the significance of that. May we have another look at that slide, please?

(Slide)

KAY: You see those spots seem to be in rows of four. There is one right in the middle there. Two are dark and two are lighter.

STROMBERG: I see more than four and less than four in a row. At this time, I do not think that there is any significance to the number.

KAY: You see the groups of four here—some are dark and some are light. It is almost as if you had a duct leading this way and then one at right angles.

STROMBERG: While I cannot agree with you about the number of spots, I do agree with your idea concerning the darkness and lightness of the spots and the possibility that we are looking at mercury lodged at the ends of capillary pores that extend through the fibril. The dark, clearly outlined areas are probably on the side of the fibril nearest the photographic plate, and the lighter, fuzzy areas are on the side of the fibril nearer the electron gun. The fuzziness is accounted for by the additional scattering of the electrons as they pass through the fibril.

W. R. KENZIE: (Ontario Research Foundation): It seemed as though the mercury spots were in the dark areas, or fibril bands. Is that correct?

STROMBERG: You mean the periodic cross-striations?

KENZIE: Yes.

STROMBERG: Are you referring to the depression or elevation that exists in the electron micrograph of the dessicated fibril?

KENZIE: The ones I noticed were particularly in the slide we had last, where the spots seemed to be in the dark areas.

STROMBERG: What do you mean by dark areas?

KENZIE: The ones commonly called the fibril bands.

CHARLES W. MANN: (Office of the Quartermaster General, Washington, D. C.): I think what Mr. Kenzie is referring to is the denser or darker band portion. I noticed that also. I wondered if you have any explanation as to why the mercury shows up there. Does that indicate a finer structure or has the mercury been removed from the less dense areas?

STROMBERG: These spots are approximately 250 Å wide in a transverse direction and 350 Å long in the longitudinal direction of the fibril. As many as nine bands within the 640 Å period have been observed in electron micrographs of stained collagen fibrils. Dimensionally, it would be difficult to reconcile the spots of mercury with any band, but they do align themselves in neat rows and we have considered this possibility. From all the electron micrographs at hand we have not been able to make any positive determination as to the location of the spots with relation to the elevations and depressions observed in the dessicated fibrils.

W. T. RODDY: (Tanner's Council Research Laboratory). I would like to ask the speaker if the present work indicates that the internal surface of leather would be much greater than we previously knew of it from microscopic observation, where we used the diameter of the fiber as being three microns and estimated from a microscopic measurement of a series of cross sections, that there was approximately one mile of fiber per square foot of sole leather. Would the present measurements indicate that it is greater or less?

STROMBERG: Light microscopes would not resolve structure below 0.2 microns. It would seem to me, therefore, that the basic assumption made regarding the diameter of the fundamental units of collagen should be reconsidered in the light of the finer structures revealed by the electron microscope. Considering the fibril to be at least an order of magnitude smaller than the 3-micron diameter used in your calculations, the internal surface of leather would have to be much greater. In addition, the existence of pores in these fibrils would further increase the calculated value.

MAESER: Are there any other questions? If not, we will thank Dr. Stromberg again for this most interesting paper.

H. G. TURLEY: (Rohm and Haas Company) Apropos of what Dr. Roddy was talking about, it seems to me to be a question of the fact that big pores have little pores, and so on, ad infinitum.

Influence of Brining and Salt Curing on the Composition of Steer Hides

By J. JACOBS TANCOUS*

Department of Basic Science in Tanning Research
Foundation Tanners' Council Research Laboratory
University of Cincinnati

INTRODUCTION

O'Flaherty [1] published a paper on "What Really Makes Leather," and his paper pointed out that two-thirds of every hide that the tanner buys is non-leather making, and only one-third, (sometimes less), is actual leather making substance. On this basis a revaluation of hide and leather costs is desirable and tanners and shoe manufacturers should really be concerned for in few other businesses is raw material purchased on other than an analytical basis. It is most desirable in this period of economic competition.

Through interest in the paper an "Improvement in Cure Program" was set up in this laboratory to study, first, basic research concerning the tanners' raw material and, later, its application on composite samples from lots of cured hides. It was decided to study the positional variation in the fresh hide composition within a steer hide side, as well as the degree of bilateral symmetry. Since a high level of symmetry was anticipated, it was decided to study the effect of brine curing and green salting on the composition of the cured sides. Four hides were examined to secure an estimate of between hide variability. The hides used were 70 pound red haired native steer hides.

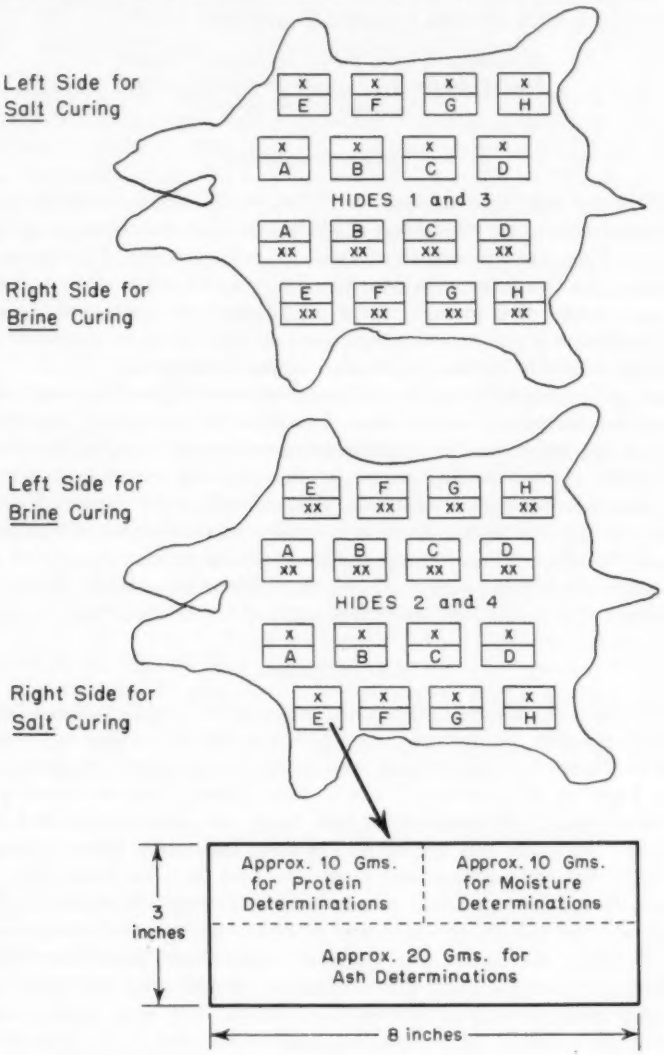
EXPERIMENTAL

The hides were obtained individually immediately after flaying and sampled as soon as possible. Specimens, 3 by 8 inches in size, were taken in 16 areas as shown in Figure I. The samples were immediately placed in plastic "food freezer bags" so moisture would not be lost. After a control sampling each hide was trimmed of excess parts, legs, head, etc., and was divided at the backbone. One side was spread on the floor and salted down with coarse salt (⅛″), fine salt (table grade) being sprinkled on a few hours later. The side was then rolled hair side out and placed in a covered crock in a refrigerator. The other side of the hide was placed in a saturated brine solution. After 24 hours, the brined side was removed, drained, rolled hair side out and placed in a covered crock in a refrigerator, no additional salt being added. The sides were allowed to cure 30 days before they were again sampled. Samples, after curing, were taken immediately adjacent to the control areas of the fresh hide.

*This report is made as part of the Improvement in Cure Program sponsored by the Hide Bureau, Tanners' Council, in cooperation with the American Meat Institute Foundation.

FIGURE 1

Diagram of Sampling of the Four Steer Hides Showing the Eight Sampling Positions on Each Side and the Detail of Each 3 x 8 Inch Specimen.



A, B, C, D, E, F, G, H — Fresh Specimens
X — Specimens to be taken after salt curing
XX — Specimens to be taken after brine curing

The position of sampling of the four hides was as illustrated in Figure I, fresh samples were taken in the near position in respect to the backbone, "A", "B", etc. in Figure I, cured samples in the far position, "x" and "xx" in Figure I, for hides 1 and 3; the fresh samples were taken in the far position, the cured sample in the near position for hides 2 and 4. Also interchanged were the brined and cured sides. Facing the head of the hide, hair side out, for hides 1 and 3, the right side was brined, the left side was salted; for hides 2 and 4, the right side was salted, the left side was brined.

By taking the samples in this manner, fresh and cured samples were cut adjacent to each other in the same hide so that direct comparisons of the data were possible. By taking the fresh and cured samples from the same hide, hidewise variation was avoided; and if bilateral symmetry could be established for the fresh sides, then results of brined versus salted sides could be compared directly.

Each sample, which had been placed in a plastic bag, was prepared for analysis the same day it was cut from the hide. The hair was clipped very close with a small animal clipper; the flesh was removed with a sharp knife. The samples were not washed since previous work showed that non-protein nitrogen is lost by washing the samples. A quarter inch edge was trimmed off of the sample before it was divided, as shown in Figure I, for various analyses.

About 10 grams were taken for protein analysis. This sample was sealed in a plastic bag, was preserved in a deep freeze unit at 0°F. and was used for a complete protein fractionation which was run in duplicate. The method used for determining the protein constituents was that developed by the author [2] and four fractions were obtained. Hair, epidermis, elastic tissue and unextractable globular proteins are reported in fraction I; extractable globular proteins composed of entities referred to as albumins, globulins and mucoids (coagulable proteins) in fraction II; collagen in fraction III; and nonproteins, as urea and amino acids, in fraction IV. Total nitrogen values were also obtained.

Two samples, about 5 grams each, were taken for moisture determination. Since it was decided that a solvent extraction [3] should be used for determining moisture and since a preliminary test showed that 24 hours extraction with benzene was a suitable method, the moisture samples, cut into six pieces each, were placed in their respective Soxhlet flasks and covered with about 100 ml. of benzene. They were set aside until they could be extracted.

Two samples, about 10 grams each were taken for ash determination. They were weighed, placed in small beakers and stored in a refrigerator until they could be ignited and ashed.

All samples taken—fresh, salt cured and brine cured—were handled in the same manner and the same analyses were run on all. After the tests were

TABLE I

Fractionation of Four Steer Hides
Fresh, Salt Cured, and Brine Cured Showing Positional Variation

		Fresh Sides		Cured Sides	
	Position	To be Salted	To be Brined	Salted	Brined
Fraction I					
Elastin	A	5.5%	5.1%	7.2%	6.7%
Keratin	B	5.5	5.1	7.2	6.7
Epidermis	C	4.8	4.5	6.0	5.5
Unextractable	D	4.8	4.6	4.9	5.6
Globular	E	7.7	6.7	8.2	7.0
Protein	F	5.7	5.3	6.2	5.8
Nitrogen	G	4.7	5.3	5.7	5.2
	H	6.0	5.5	6.3	6.7
	Av.	5.6	5.3	6.5	6.2
Fraction II					
Extractable	A	7.7	7.6	5.6	5.8
Globular	B	7.3	7.5	5.0	5.1
Protein	C	5.8	6.4	4.4	4.5
Nitrogen	D	6.0	5.6	4.0	4.1
	E	8.6	7.5	5.1	5.3
	F	6.1	6.4	4.7	4.2
	G	5.3	6.4	4.9	4.2
	H	6.8	6.2	4.8	4.3
	Av.	6.7	6.7	4.8	4.7
Fraction III					
Collagen	A	85.4	85.8	85.7	85.9
Nitrogen	B	85.9	85.9	86.2	86.6
	C	88.2	87.8	88.1	88.5
	D	87.9	88.4	89.6	88.8
	E	82.1	84.4	84.9	85.9
	F	86.8	87.0	87.4	88.4
	G	88.7	86.8	87.8	89.1
	H	85.6	86.8	87.4	87.5
	Av.	86.3	86.6	87.1	87.6
Fraction IV					
Non	A	1.4	1.5	1.6	1.6
Protein	B	1.4	1.5	1.7	1.7
Nitrogen	C	1.3	1.3	1.5	1.5
	D	1.3	1.4	1.6	1.5
	E	1.7	1.5	1.9	1.7
	F	1.4	1.4	1.7	1.6
	G	1.4	1.4	1.6	1.4
	H	1.6	1.5	1.6	1.6
	Av.	1.4	1.4	1.7	1.6

NOTE: Each result expressed above is the average of eight results, four sides tested in duplicate, and represents the percentage of the total nitrogen that is in a fraction.

completed, statistical analyses were made on these data to determine the degree of confidence on the results concerning the degree of bilateral symmetry, hidewise variation, positional variation and the variation of fresh hide due to brine and salt curing.

Results

A summary of the results are given in Tables I to IV. The individual data are not given but are available [4]. Tables I and II give average values for the four fractionations of the samples. Tables III and IV give average values for ash, moisture, total nitrogen, hide substance and collagen hide substance.

TABLE II

Fractionation of Four Steer Hides
Fresh, Salt Cured, and Brine Cured Showing Hidewise Variation

		Fresh Sides		Cured Sides	
	Hide	To be Salted	To be Brined	Salted	Brined
Fraction I					
Elastin	1	4.9	4.1	6.3	5.8
Keratin	2	5.4	4.9	6.2	6.2
Epidermis	3	6.2	5.9	7.2	7.3
Unextractable	4	5.9	6.2	6.2	5.3
Globular	Av.	5.6	5.3	6.5	6.2
Protein					
Nitrogen					
Fraction II					
Extractable	1	5.5	5.7	5.1	4.5
Globular	2	6.8	7.3	4.6	5.0
Protein	3	6.9	6.8	4.5	4.7
Nitrogen	4	7.5	7.0	4.9	4.5
	Av.	6.7	6.7	4.8	4.7
Fraction III					
Collagen	1	88.6	89.1	86.8	88.2
Nitrogen	2	86.1	86.2	87.6	87.3
	3	85.4	85.8	86.7	86.3
	4	85.1	85.2	87.3	88.6
	Av.	86.3	86.6	87.1	87.6
Fraction IV					
Non	1	1.0	1.1	1.8	1.5
Protein	2	1.7	1.6	1.6	1.5
Nitrogen	3	1.5	1.5	1.6	1.7
	4	1.5	1.6	1.6	1.6
	Av.	1.4	1.4	1.7	1.6

NOTE: Each result expressed above is the average of sixteen results, eight positions tested in duplicate, and represents the percentage of the total nitrogen that is in a fraction.

TABLE III

Moisture, Ash, Nitrogen, Hide Substance, and Collagen Hide Substance Contents for Four Steer Hides, Fresh, Salt Cured, and Brine Cured Showing Positional Variation.

		Fresh Sides		Cured Sides	
	Position	To be Salted	To be Brined	Salted	Brined
Moisture	A	63.0%	64.2%	45.9%	49.6%
Content	B	62.4	63.3	44.8	51.0
	C	62.1	61.7	42.4	46.3
	D	62.0	61.2	41.7	46.3
	E	65.2	63.7	46.2	49.7
	F	62.2	62.2	45.1	49.6
	G	61.2	62.8	45.3	47.9
	H	62.4	63.7	43.9	47.4
	Av.	62.6	62.9	44.4	48.5
Ash	A	0.821	0.838	15.11	10.44
Content	B	0.764	0.872	14.85	10.55
As	C	0.680	0.705	13.94	10.31
Received	D	0.610	0.621	13.77	9.56
Basis	E	0.881	0.952	15.75	10.62
	F	0.867	0.889	14.72	11.18
	G	0.745	0.746	14.59	11.04
	H	0.724	0.761	15.04	10.52
	Av.	0.762	0.798	14.72	10.53
Total	A	5.54	5.49	6.10	6.01
Nitrogen	B	5.78	5.83	6.53	6.33
As	C	6.00	5.82	6.98	6.56
Received	D	5.80	5.83	6.75	6.52
Basis	E	5.36	5.66	6.08	6.28
	F	5.82	5.90	6.77	6.24
	G	5.94	5.75	6.42	6.57
	H	5.57	5.68	6.63	6.32
	Av.	5.73	5.75	6.53	6.35
Total	A	31.1	30.9	34.2	33.8
Hide	B	32.5	32.8	36.7	35.6
Substance	C	33.7	32.8	39.3	36.9
As	D	32.6	32.8	38.0	36.7
Received	E	30.1	31.8	34.2	35.3
Basis	F	32.8	33.2	38.1	35.1
	G	33.4	32.4	36.1	36.9
	H	31.3	31.9	37.3	35.5
	Av.	32.2	32.3	36.7	35.7
Collagen	A	26.6	26.5	29.3	29.2
Hide	B	27.9	28.2	31.6	30.7
Substance	C	29.7	28.7	34.6	32.7
As	D	28.6	28.9	34.1	32.8
Received	E	24.8	26.8	29.0	30.2
Basis	F	28.4	28.8	33.3	31.0
	G	29.6	28.1	31.7	33.0
	H	26.3	27.7	32.5	30.9
	Av.	27.8	28.0	32.0	31.3

NOTE: Each result expressed above is the average of eight results, four sides tested in duplicate.

TABLE IV

Moisture, Ash, Nitrogen, Hide Substance, and Collagen Hide Substance Contents for Four Steer Hides, Fresh, Salt Cured, and Brine Cured Showing Hidewise Variation.

		Fresh Sides		Cured Sides	
	Hide	To be Salted	To be Brined	Salted	Brined
Moisture Content	1	62.3%	63.0%	43.4%	48.6%
	2	64.5	63.0	44.7	47.8
	3	61.1	64.0	45.5	50.4
	4	62.4	61.7	43.9	47.1
	Av.	62.6	62.9	44.4	48.5
Ash Content As Received Basis	1	0.654	0.665	14.98	10.66
	2	0.816	0.937	14.98	10.40
	3	0.800	0.759	14.82	10.90
	4	0.777	0.831	14.12	10.16
	Av.	0.762	0.798	14.72	10.53
Total Nitrogen As Received Basis	1	5.51	5.57	6.24	6.16
	2	5.68	5.79	6.14	6.22
	3	5.80	5.82	6.66	6.36
	4	5.92	5.82	7.09	6.68
	Av.	5.73	5.75	6.53	6.35
Total Hide Substance As Received Basis	1	31.0	31.4	35.2	34.7
	2	32.0	32.5	34.5	35.0
	3	32.6	32.7	37.4	35.7
	4	33.3	32.7	39.8	37.5
	Av.	32.2	32.3	36.7	35.7
Collagen Hide Substance As Received Basis	1	27.5	28.0	30.6	30.6
	2	27.6	28.1	30.3	30.6
	3	27.9	28.0	32.5	30.8
	4	28.4	27.9	34.8	33.3
	Av.	27.8	28.0	32.0	31.3

NOTE: Each result expressed above is the average of sixteen results, eight positions tested in duplicate.

The results in Tables I and III were averaged according to positions—A, B, C, D, E, F, G and H— and according to stock types—fresh sides to be salted, fresh sides to be brined, salted sides, and brined sides. Each result, then, is the average of eight determinations, four sides tested in duplicate. These tables are given to show the symmetry between the sides of the fresh stock and the change in the stock due to brining and salt curing. They also show the variations between positions.

The results in Tables II and IV were averaged according to hides—1, 2, 3 and 4—and according to stock types—fresh sides to be salted, fresh sides to be brined, salted sides, and brined sides. Each result in these tables is

the average of sixteen determinations, eight positions tested in duplicate. These tables show the variation between hides.

More valid interpretations of Tables I to IV can be given from the results of the statistical analyses than from the data themselves. The tables concerning the statistical analyses are not given in this report but are available [4]. (Complete analyses were done on individual data for sides, not on averages.) The results of the statitical analyses are as follows:

Bilateral Symmetry

To determine the degree of bilateral symmetry in the fresh hides a t-test of the chemical analyses was used to compare the means of the left and right sides of each hide. The results showed that there was bilaterial symmetry for all four hides. This was true for ash, moisture, total nitrogen, and the four nitrogen fractions—elastin, keratin, epidermis, and unextractable globular protein nitrogen, extractable globular protein nitrogen, collagen nitrogen and non-protein nitrogen. This bilateral symmetry about the backbone refers to left and right sides as a whole. Individual positions were not tested for symmetry.

Positional Variation and Hidewise Variation

In considering the data on the fresh, brined and salted sides by statistical analyses, it was realized that there were three factors to be handled—hides, cure types and positions. There were four hides analyzed; there were three types of cure analysed, that is, fresh, brine cured and salt cured; and there were eight positions analysed for each side of the four hides. Thus for testing the data, a three factor analysis was used for each of the determinations—moisture, ash, total nitrogen, and the four nitrogen fractions.

The results of the three factor analysis showed that there were significant variations between positions and also between hides. As would be expected there were significant variations between stock types, that is, between fresh, brine cured and salt cured sides. These variations, hidewise variation, positional variation and stock type variation, were true for ash, moisture, total protein nitrogen contents, and four nitrogen fractions.

For the interaction of factors, from the results of the three factor analysis, the stock type-hide interaction was the only one that was significant. This indicates that there is a variation in curing which is influenced by the variation in hides. Since this interaction is significant, more hides should be obtained and analysed before a valid sampling plan can be obtained.

Comparison of Fresh Sides with Salt Cured Sides

A t-test was used to compare the fresh sides with the salt cured sides; this showed that the moisture contents were significantly decreased from an

average of 62.6 per cent in the fresh sides to 44.4 per cent in the salt cured sides; that the ash contents were significantly increased from an average of 0.762 per cent in the fresh sides to 14.72 per cent in the salt cured sides; that the total nitrogen contents were significantly increased from 5.73 per cent in the fresh sides to 6.53 per cent in the salt cured hides. Considering the protein nitrogen fractions, there was a *significant* increase in the collagen nitrogen fraction and the non protein nitrogen fraction after salt curing compared to the fresh sides. There was no significant change in the extractable globular protein nitrogen (significance level of the decrease found was 0.1 – 0.05) or the elastin, keratin, epidermis and unextractable globular protein nitrogen, after salt curing compared to the fresh sides.

Comparison of Fresh Sides with Brine Cured Sides

A t-test was used to compare the data for the fresh sides with the brine cured sides and the results showed that the moisture contents were significantly decreased from an average of 62.9 per cent in the fresh sides to 48.5 per cent in the brine cured sides; that the ash contents were significantly increased from an average of 0.789 per cent in the fresh sides to 10.53 per cent in the brine cured sides; that the total nitrogen contents were significantly increased from an average of 5.75 per cent in the fresh sides to 6.35 per cent in the brine cured sides. Considering the protein nitrogen fractions, there were significant increases in the collagen nitrogen and non protein nitrogen. The extractable globular protein fractions decreased significantly after brine curing compared to the fresh sides. There was no significant change in the elastin, keratin, epidermis, and unextractable globular protein fraction after brine curing compared to the fresh sides.

Comparison of Brine Cured Sides with Salt Cured Sides

A t-test was used to compare the brine cured sides with the salt cured sides and the results show that there was a significant difference in the moisture contents. The average moisture for the brined sides was 48.5 per cent and for the salted sides was 44.4 per cent. This indicates that brining produced hides with higher moisture than salting. There was also a significant difference in the ash contents. The average ash content for the brined sides was 10.53 per cent and for the salted sides was 14.72 per cent. There was no significant difference in the total nitrogen contents or any of the four nitrogen fractions for the brined sides compared with the salted sides. *However, this applies to the experimental hides only and may not apply to curing in general, as this experiment was conducted under ideal conditions in the laboratory.*

Total Hide Substance, Collagen Hide Substance

Total hide substance figures, calculated by multiplying the total nitrogen

figures by the hide substance factor, 5.62, are shown in Tables III and IV. Collagen hide substance was calculated and is given in Tables III and IV. To obtain these figures, the total hide substance results were multiplied by the collagen nitrogen percentages found by protein fractionation and given in Tables I and II. Collagen hide substance figures show the amount of material accounted for as leather making substance—collagen. Taking the average figures for the four hides, the total hide substances for fresh, salt cured and brine cured hides are 32.3, 36.7 and 35.7 per cent; the collagen hide substances are 27.9, 32.0, and 31.3 per cent; the differences are 4.4, 4.7, and 4.4 per cent, respectively. It is seen that collagen hide substance is about 4.5 per cent less than the total hide substance, the 4.5 per cent being elastin, keratin, globular proteins and non proteins, for which the role in leather is unestablished.

Liquor Analysis

An analysis by fractionation was also run on the liquors from hides 2 and 3. Both the spent brine solutions from the brined sides and the run off brines from the salted sides were analysed for globular protein, non protein nitrogen and collagen nitrogen. The results were roughly calculated on the hide basis and thus are expressed as the percentage of the total hide nitrogen in the liquor. The globular protein nitrogen values from the brined sides 2 and 3 were 1.73 and 2.01 per cent and from the salted sides were 0.75 and 0.97 per cent; the non protein nitrogen values from the brined sides were 0.40 and 0.56 and from the salted sides were 0.10 and 0.14 per cent; and the collagen nitrogen values from the brined sides were 0.10 and 0.01 per cent and from the salted sides were 0.03 and 0.00 per cent, respectively. The liquors, by these analyses, contained mostly globular proteins and about twice as much globular proteins were removed from the brined sides as from the salted sides. There were very small amounts of collagen nitrogen and non-protein nitrogen in the liquors from these two curing methods.

Table II gives the extractable globular protein nitrogen values for the fresh sides. The values for sides 2 and 3 to be brined were 7.3 and 6.8 per cent and for the sides to be salted were 6.8 and 6.9 per cent, respectively. This is expressed as the percentage of the total nitrogen that is in the globular protein nitrogen fraction.

If the amount of the total globular proteins removed by brining and salting are calculated, it is noticed that there was 23.7 and 29.6 per cent of the globular proteins removed in the brine liquor for hides 2 and 3 and there was 11.0 and 14.1 per cent removed in the brine taken from the salted hides 2 and 3. About one-fourth of the globular proteins were removed by brining and about one-eighth were removed by salting. It will be recalled that the hide fractionation data showed a statistically significant decrease in the globular protein nitrogen content as a result of brining but did not do so for the salted sides.

Discussion Concerning Leather Making Substance

According to O'Flaherty [1] only one-third of the weight of cured hide that the tanner buys is collagen. The results showed this to be true for the laboratory cured hides. Although 87.1 and 87.6 per cent of the total nitrogen of the salted and brined sides, respectively, was collagen nitrogen, only 32.0 and 31.3 per cent of the total weight of the cured sides was collagen protein; this is about one-third of the weight, the balance being moisture, salt and fat, etc. These results represent ideally cured hides; poorly cured hides may contain even less leather making substance.

Summary

1. Bilateral symmetry in paired sides, exists for fresh hides. This has been established from the results on moisture, ash, total nitrogen and the four nitrogen fractions—elastin, keratin, epidermis and unextractable globular protein nitrogen, extractable globular protein nitrogen, collagen nitrogen and nonprotein nitrogen.

2. Within any given side there are significant variations due to position. This was true for moisture, ash, total nitrogen and the four nitrogen fractions.

3. Between hides there were significant variations. This was true for moisture, ash, total nitrogen and the four nitrogen fractions.

4. Salting and brining significantly changed the moisture, ash, total nitrogen and some of the nitrogen fractions when compared with the fresh stock.

5. There was no significant difference between salting and brining when the two curing methods were compared with each other, except for moisture and ash. Brining produced a hide with higher moisture content than green salting. Less ash was obtained from the brined hides, than from the salted hides. (Ash is a reflection of the sodium chloride content.)

6. There was a significant interaction, the cure type-hide interaction, which indicates that there is a variation in curing which is influenced by the variation in hides.

7. There are not enough data to establish the best position for sampling.

8. Collagen hide substance was always about 4.5 per cent less than total hide substance, the 4.5 per cent being globular proteins, elastin, keratin and non-protein.

9. Only one-third of the weight of cured hides is collagen hide substance.

10. More globular proteins were removed in the brine solution from the brined sides than in the run-off liquor from the salted sides.

Conclusions

In conclusion it can be stated from the results of the work on the four hides that bilateral symmetry does exist in fresh hides. Positional variations and hidewise variations also exist, so before a simple work methods can be developed to study cured hide composition a representative sampling position must be established.

Acknowledgments

The author expresses thanks to Miss Hsiao May Wu for technical assistance in completing the analytical and the statistical analyses and to Dr. Robert M. Lollar for guidance on the statistical analyses.

Bibliography

1. O'Flaherty, F., *Leather and Shoes*, Sept. 3 (1949).
2. Jacobs, J. L., *J. Amer. Leather Chemists Assoc.*, **44**, 722 (1949).
3. Kremen, S. S. and Lollar, R. M., *ibid*, **46**, 34 (1951).
4. Wu, Hsiao May., Master's Thesis, University of Cincinnati (1951).

Received March 28, 1955.

ABSTRACTS

Activated Sludge and Filters for Tannery Wastes Treatment. By E. S. Chase and P. Kahn. *Wastes Engineering*, **26**, 167 (1955). The investigations and experiences relating to the treatment of tannery and wool scouring wastes at a sheepskin tannery (in Eastern Massachusetts), now no longer in operation, are described. In addition, a brief account is given of what is probably the first instance in this country of the privately sponsored control and regulation of the sanitary condition of a public stream. Pilot plant studies began in May 1914 and continued through February 1917. Two pilot installations were made, one a trickling filter, and the other a small activated sludge plant. The trickling filter studies were completed in October 1915, and the activated sludge studies were begun in December 1915 and finished in February 1917. These studies were made on the tannery wastes combined with the partly degreased scouring wastes. The pilot plant was constructed and operated at an initial rate of 591,500 gallons per acre per day, equivalent to 8,560 gallons per day on the filter. It was also operated at 870,200 and 925,800 gad* during the experiments. Removal of putrescible organic matter by the filter and humus tank varied between 51 and 71 per cent by the oxygen consumed test, and between 53 and 73 per cent by the albuminoid ammonia determination. Fats and suspended solids reduction varied between 60 and 95 per cent. Operations at a rate of 900,000 gad were unsatisfactory. the dissolved oxygen in the effluent at this dosing rate varied between 20 and 35 per cent saturation compared with 91.6 per cent saturation at a dosing rate of 600,000 gad. Stability tests also indicated the 900,000 gad rate to be too high and a filtration rate of

* Gallons per acre per day.

750,000 gad was therefore recommended. Experiments on the destruction of psychoda indicated that about 1,000 ppm. free chlorine added in solution would probably accomplish the desired results without seriously affecting the efficiency of the filter. Operation of the filter during the winter was feasible. Although the filter effluent was darker in color, more turbid, and putrecible, dilution with five to ten volumes of reservoir water made it nonputrecible and satisfactory in appearance and odor. Under proper conditions, the activated sludge process, as developed on a pilot plant scale, was able to render the tannery wastes entirely suitable for discharge into Hawes Brook and the Neponset River. An effluent was produced which was practically clear, free from objectionable odor, and perfectly stable. During a period of over four months, between March and July 1916, the following reductions were obtained: Albuminoid Ammonia: Dissolved 80 per cent; Suspended 69 per cent; Free Ammonia Nitrogen 65 per cent; Suspended Solids, Total 78 per cent; Fats by Ether Extraction 79 per cent. Due to the variability of the wastes it was found necessary to equalize their flow and quality in order to prevent destruction of the bacterial activity of the sludge, and to make the wastes more amenable to treatment. Milk of lime was added periodically to prevent an acid effluent from the equalizing tank, and to maintain the alkalinity level of the wastes above the minimum required for good clarification. Return activated sludge, as high as 50 per cent of the influent was found to be quite economical when compared with relative quantities of air required per gallon of wastes treated. Within certain limits it was found that the rate of air supply and the period of aeration could be considered inversely proportional, with economic advantages favoring longer periods of aeration. The pilot plant operation indicated that under the most economic use of air, the volume of sludge to be disposed of would probably not exceed 10,000 gal. per million gallons of wastes treated. This sludge could be dried on sludge beds, if applied in shallow doses not over ten inches deep, due to its slow drying qualities. The major drawbacks of the trickling filter were the dissemination of foul odors due to the spraying of the liquid on the filter, and the breeding of psychoda flies. The activated sludge process did not present these drawbacks. The relative quantities of sludge produced by either process were comparable, activated sludge being somewhat larger in volume but lower in solids content due to digestion of organic matter. Estimated construction costs (1917) for two full-scale plants were approximately the same ($62,000 and $63,000). However, the activated sludge plant had additional power requirements for producing compressed air. Total annual costs of treatment, including fixed charges, were estimated to be $24,000 for the trickling filter process, and $34,000 for the activated sludge process. The tannery at the time the pilot plant investigation began, had already in service settling tanks and sand filters of inadequate capacity and efficiency. An inefficient acid-cracking plant for the wool scouring wastes was also in use. In view of the costs involved in installing either activated sludge or trickling filters, although either was practical, it was decided to make improvements and enlargements of the then existing facilities. These consisted of additional settling tanks, improved sand filters, and considerable additions to the degreasing plant. Supervision of the improved treatment works was maintained until the completion of a Metropolitan trunk sewer in August 1929 and the discharge of wastes therein. Complete operational and analytical data were maintained. The analytical data from the year 1925 are given as typical operations at the tannery for the degreasing and wastes treatment plants and for conditions in the Neponset River. The wool scouring wastes, approximately 25,000 gal. daily were conducted to tanks for sedimentation and cooling, from whence the settled wastes were pumped to acid-cracking tanks to be acidified with sulfuric acid. The precipitated grease was permitted to either settle on the bottom or rise as scum to the top, after which the clarified middle liquor was drawn off to be added to the combined wastes from the tannery. The sludge from the sedimentation tanks was pumped to the sludge beds, together with the combined tannery wastes sludge. After several repeated filling and settling cycles in the acid-cracking

tanks, the acid sludge was drawn off to dewatering beds. The "magma" remaining, after draining and drying, was then wrapped in burlap to form "puddings" which were steam heated in hydraulic presses, where the grease was melted and pressed out leaving a fairly dry thin cake which could be used as a fertilizer. The oil was further separated by flotation and refined by boiling with sulfuric acid, forming "acid wool degras" for sale. During the year 7,948,171 lb. of wool were scoured over a 307-day working year. A total of 674,500 gal. of sludge was produced during the year in the sedimentation tanks, which analyzed 92 per cent water, 8 per cent dry solids of which 45 per cent were fats. By exercising closer chemical controls the alkalinity of the wastes was decreased with a corresponding reduction in the amount of sulfuric acid required for cracking. For example, in 1920 100.9 lb. of acid were required per 1,000 gal. of liquor compared with 47.5 lb. in 1925. The total quantity of grease sludge produced from acid cracking for the year 1925 was 456,600 gal., somewhat below the average for the previous ten years. This amounted to 68.0 gal. per thousand gallons of scouring liquor treated. Laboratory tests indicated that heating of the grease sludge, before drawing to the magma beds, decreased the time required for dewatering. Live steam was therefore admitted to the cracking tanks during the winter through the air line used for mixing the acid and settled scouring liquors. This reduced the dewatering time and permitted more water to drain away before the magma froze in the winter. A total of 674.10 cu. yd. of magma was produced during the year, a reduction of 70 per cent by volume in drying. The magma "puddings" were pressed to produce 151,570 lb. of degras, an average of 22.5 lb. per thousand gallons of scouring liquor treated. The degras, as produced, contained 98.66 per cent grease, most of the remainder being moisture. This was sold at a price averaging $0.04 per pound, for a total of $5,268.40. The cost of operation of the degreasing plant had decreased steadily due to reduction in the costs of materials and to more efficient operation. Total costs for the year 1925 were $10,213.02, approximately one-half the cost during the period 1918-1920, based on the same amount of wool scouring effluents treated.

Wastes from the tannery and the previously described settled and acid-cracked wool scouring liquors from the degreasing plant, averaging between 400,000 and 600,000 gpd., were collected and pumped to sedimentation tanks. During periods of warm weather and low stream flow, sedimentation tank effluent was treated by chemical precipitation with alum, being controlled at a pH of 5.2 with sulfuric acid. The chemical effluent was treated by intermittent sand filtration up to the capacity of the area available, and the remainder was diluted in Hawes Brook with water drawn from the reservoir. The sludge from sedimentation and chemical precipitation was dewatered on sludge beds and either dumped on wasteland or used for fertilizer. The average flow of waste to the treatment plant during 1925 averaged 588,900 gal. per working day. Secondary treatment with alum was required on 134 working days. The following table illustrates the effectiveness of sedimentation, chemical precipitation and sand filtration during the summer months.

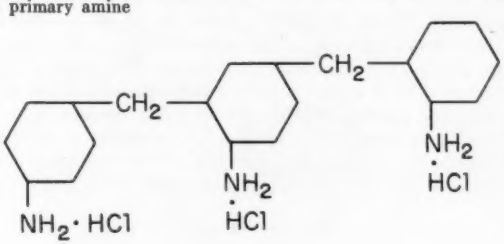
	Average analyses, ppm.				Percentage reduction by			
Constituents (total)	Crude wastes	Sed. tank effluent	Chemical effluent	Filter effluent	Sedimentation	Chemical precipitation	Filter beds	Overall treatment process
Oxygen consumed	678	357	242	72	47.4	32.2	70.3	89.4
Albuminoid nitrogen	24.6	11.5	7.8	1.6	53.2	32.2	79.5	93.5
Residue on evaporation	2,995	2,008	1,850	1,659	32.9	7.9	10.3	44.7
Disolved Solids	1,681	1,755	1,802	.....	4.4	2.7	.....	.....
Suspended solids	1,314	253	48	.....	80.8	81.5	.....	96.3*
Fats	439	157	47	28	64.2	70.1	40.4	93.5

*Reduction by sedimentation and chemical precipitation alone.

Sludge volumes of 2,621,000 and 965,000 gal. were produced by initial sedimentation and chemical treatment, respectively during 1925 with the following average analyses: Sedimentation without alum; 6.9 per cent dry solids, 67.1 per cent organic matter in the solids and 35.6 per cent fats in the solids; Secondary treatment with alum; 3.7 per cent dry solids, 65.2 per cent organic matter in solids, 34.4 per cent fats in solids. During 1925 all wastes not filtered received an average dilution of 15 volumes of reservoir water before discharge to Hawes Brook. Rinse waters were treated by passing through a perforated plate screen before admitting them to Hawes Brook. On the average working day, 283,000 gal. of rinse water were thus treated in 1925. A total wastes and rinse water flow per average working day was 870,900 gal. The rinse waters had an average oxygen consumed of 79 ppm., albuminoid nitrogen of 2.4 ppm., total solids of 285 ppm., and suspended solids of 79 ppm. in 1925. The total cost of operation of the wastes treatment plant, excluding the degreasing plant costs, supervision, laboratory, and overhead, was $10,530.26 for the year 1925. This approximated $58.24 per million gallons of wastes treated, and was within $600 of the previous 10 years' average annual operating costs. This figure could be apportioned to the various phases of treatment as follows: collection and pumping 26.3 per cent; tank treatment 43.4 per cent; sludge disposal 16.1 per cent; filter beds 8.4 per cent; miscellaneous 5.8 per cent. Over the years, during the warmer months, weekly inspections of the Neponset River were maintained. Observations were made, samples collected, and analyses carried out. Based on the results of these inspections, adjustments in degree of treatment were made to maintain the river in as unobjectionable condition as possible. During unusually dry and hot summers it was found necessary to add nitrate to provide essential oxygen. This was probably the first example in this country of the use of sodium nitrate in stream sanitation. This statement applies also to the program of stream inspection and regulation of treatment by other than a public agency. J. F. W.

Cationic Tannins. By K. Rosenbusch. *Das Leder*, **6**, 1 (1955). An attempt was made to synthesize a true cationic tannin. Amphotannins are cationic compounds in acid solution, but are not cationic tannins. First an attempt was made to change a commercial high polymer, polymethacrylic acid amide, to its amine by the Hofmann reaction with hypobromous acid, but most of the amide was saponified and the product had only an anionic tanning action. A Novolak free from hydroxyl groups was made by condensation of benzyl chloride by the Friedel-Crafts reaction, then nitrating the product. This Novolak was not soluble in the usual organic solvents. A cationic tannin was, however, prepared as follows: An aminoplast

was made by the method of K. Frey [*Helv. Chim. Acta* 18, 491 (1935)], and then was changed to the primary amine



by thermal rearrangement at 170°-180°. The yellowish-brown thermoplastic resin was very hygroscopic; it was precipitated from aqueous solution by alkali as a white flocculent precipitate that was readily soluble in acid, but insoluble in alkali. The synthesis and rearrangement were combined by melting together the mixed hydrochlorides of aniline and ethanolamine at 170° C., then adding 1 mol of paraformaldehyde, keeping the temperature below 200°. Aniline could be replaced by toluidine or xylidine, the ethanolamine by other aliphatic bases and the paraformaldehyde by benzaldehyde or chloral, the only requirement was that the amine salts must fuse with each other. The structure of one of the products indicted that the aliphatic base did not take part in the reaction. Aniline hydrochloride has a high melting point and could not be melted without considerable loss by volatization, but this loss could be prevented and a clear melt obtained at 170° by adding one fifth of its amount of glycerine. Condensation by stirring in 1 mol of paraformaldehyde then gave the same resin as before. The resin, because of its positive charge, precipitated anionic materials such as chromate liquors, vegetable tannins, anionic syntans, sulfonated oils etc. It could be drummed into hide in acid solution, then precipitated and fixed by treatment with soda as in chrome tanning. A better method was to add neutral, insoluble resin which withdrew acid from the nonastringent tannin so that both astringency and tannin concentration were increased, however, it was necessary to add soda to complete the tanning. Fixation of resin probably was by formation of hydrogen bonds between the amine groups of the resin and polypeptide chain of the collagen. Bright yellow leather was produced with the aniline resin, chrome colored with benzaldehyde and deep brown with chloral resin. The leather darkened in light. The free aromatic amino groups could be diazotized then coupled to various components to get all shades of azo dyes. Dyeing of the resin tanned leather was accomplished by either dipping it in a 1 per cent acid nitrite solution or brushing on this solution, (cooling was not required) then applying the coupling component in the same manner. The latter may be phenols or aromatic amines in weak alkaline or acid solution. I. D. C.

Hide and Skin Markets of the World. By W. Freudenberg. *Das Leder,* **5,** 12, 35, 64, 88, 109, 135, 155, 189, 222, 255, 293 (1954); **6,** 9, 64 (1955). See This Jour., **49,** 532. A description of the kinds, numbers, quality, and grades of hides and skins produced in America, Asia, and Europe. I. D. C.

Surface Chemistry of Synthetic Protein Analogues. IV. By T. Isemura and K. Hamaguchi. *Bull. Chem. Soc. Japan,* **27,** 339 (1954). The surface pressure and surface viscosity of the spread monolayers of the copolypeptide of L-lysine, L-leucine and L-glutamic acid and of poly L-glutamic acid were measured in relation to substrate pH. The F-A curves in the range of pH 5.8 and 9.4 were of condensed type, but at both outsides of this pH range they were of expanded type. The area at constant pressure or surface viscosity against pH curves were of W-shape and a maximum appeared at pH 7. That the isoelectric point of the copolypeptide may lie at pH 7 was concluded from the observations of the monolayer properties. The W-shaped curve could be interpreted in terms of the ionization degree of amino and carboxyl groups. At the isoelectric point, pH 7, the surface viscosity became maximum. This is in contrast to the bulk viscometric behavious of polyampholytes. The area at constant pressure or surface viscosity and the pressure at constant area decreases rapidly if the pH of the substrate exceeds 4.6. This fact corresponds to the viscometric behaviour of electrolytic polypeptides in solution, i.e., when the elongation of a molecule by the electrical repulsion of ionized groups occurs, the rapid increase in viscosity and in solubility appears in solution and at monolayer, respectively. I. D. C.

whether you tan for.....

or.....

NOPCOLENES GIVE YOU *Balanced Performance*

Since 1940, when the cationic (positive) and nonionic (neutral) emulsifiers were added to the already existing group of anionic (negative) emulsifiers, the tanning industry has shown a rapidly increasing ability to control the exact properties a fatliquor can give to each type of leather.

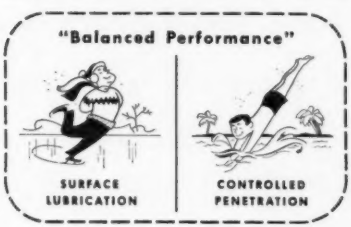
This progress has been further accelerated by the realization that a proper understanding of the charges on the surface of a given leather (i.e., whether they are positive or negative) is of even greater importance than the actual pH conditions which exist.

As a result, it is possible today to balance the cationic and anionic charges to yield fatliquors with (1) low moisture content for economy, (2) the highest percentage of neutral oil for lubricating and fulling, and (3) controlled penetration.

As you would expect, Nopco, whose very earliest research was in fatliquors, continues to put this knowledge to work for you in producing ever finer, more sensitively controlled Nopcolenes®.

Write today for your FREE copy of the Nopcolene booklet, containing up-to-the-minute data and tannery-tested formulas for use with various leathers.

Nopco Chemical Co., 346 Bark St., Harrison, N. J.



NOPCO

PLANTS: Harrison, N. J.
Cedartown, Ga. • Richmond, Calif.
London, Ont. Canada

BIOBATE

- Biobate is a highly standardized bating compound of extreme stability.
- Biobate provides controlled, effective enzyme action during bating for all types of leather.
- Biobate is adaptable to all bating conditions and procedures.

SEBACOL

for dependable unhairing

Sebacol produces clean, uniform quality leather under varied beamhouse practices.

STEROZOL

reliable germicide

Sterozol inhibits bacterial action and mold growth on raw stock and leather in process.

WALLERSTEIN COMPANY, INC. • 180 MADISON AVENUE, NEW YORK 16, N.Y.

Highest Quality

SODIUM SULPHIDE FLAKES

Our flakes dissolve into a PALE YELLOW SEDIMENT FREE solution, denoting an absence of IRON and other heavy metals. LEATHER MANUFACTURERS are especially pleased with our WATER THIN flakes because these flakes need not be pre-dissolved before using.

MANUFACTURED BY

BARIUM REDUCTION CORPORATION

SOUTH CHARLESTON, WEST VIRGINIA

BORNEO **CUTCH** EXTRACT

(MANGROVE BARK EXTRACT)

SAXE CUTCH CORPORATION

500 FIFTH AVENUE NEW YORK 36, N. Y.

Mardol TANNERY OILS

TANNERY OILS AND FAT LIQUORS FOR ALL TYPES OF LEATHER

MARDEN-WILD CORPORATION

500 COLUMBIA STREET, SOMERVILLE, MASS.
MARDEN-WILD OF CANADA LTD., HALIFAX, N. S.

FASTER LEATHER PROCESSING...

. . . And tougher, more durable leather! Tanners and finishers find they get both when they use Sun's Leather-Processing Oils. For these oils mix easily and their action is fast—stepping up production, cutting out delays. Leather is better, too, uniform in quality, temper and tensile strength. For more information, call your nearest Sun Office . . . or write SUN OIL COMPANY, Philadelphia 3, Pa. *In Canada:* Sun Oil Company Ltd., Toronto and Montreal.

INDUSTRIAL PRODUCTS DEPARTMENT

SUN OIL COMPANY SUNOCO

PHILA. 3, PA. • SUN OIL COMPANY LTD., TORONTO & MONTREAL

Warner

BELL-MINE LIME

Year-round Uniformity
Dependable Source of Supply

WARNER COMPANY

Bellefonte Division, Bellefonte, Pa.

PITTSBURGH - - - - PHILADELPHIA - - - - NEW YORK

THE OHIO LEATHER CO.

Quality Calf Leather

LUXOR - BLACK JETTA
KAFFORITE - KOZY - JILL JETTA
EMBOSSED CALF - WHITE WASHETTE

TANNERY & GENERAL OFFICES: GIRARD, OHIO
BOSTON • NEW YORK • ST. LOUIS • CHICAGO

EISENDRATH FINE CALF LEATHERS

IN COLORS AND BLACK

B. D. Eisendrath Tanning Company

801 Merchandise Mart, Chicago, Ill. • Tannery at Racine, Wisconsin

92 South St., Boston, Mass., Day Gormley Leather Co. 29 W. 36th St., New York City, Eugene Williams

EST. 1908

MORITE BRAND

Sulphonated and Compounded

OILS

EST. 1908

WHITTEMORE-WRIGHT COMPANY, INC.

62 ALFORD ST. CHARLESTOWN DISTRICT BOSTON, MASS.

PRESTO

The Original Dry Color
for Splits and Suede
(also in paste form)

PRESTO COLOR COMPANY
WEST ALLIS 14, WIS.

Dry Colors ❖ ❖ Finishes

BORAX AND BORIC ACID HAVE LONG BEEN USED IN THE TANNING AND FINISHING OF GOOD LEATHER

When you want **BORAX**

or want **BORIC ACID**

SEND TODAY
FOR FREE BOOKLET:
"PROCESSING HEAVY LEATHER"

Think first of **PACIFIC COAST BORAX CO.**

DIVISION OF BORAX CONSOLIDATED, LIMITED
NEW YORK • LOS ANGELES • CLEVELAND • CHICAGO

Distributors located in principal cities throughout the U.S.A.

REILLY-
WHITEMAN-
WALTON CO.

CONSHOHOCKEN, PA.

THE LEATHER MANUFACTURER

ESTABLISHED 1883

Exclusively a Tannery Paper

Devoted to Leather Technology, Tanning and Finishing of Leather, Tannery News and Markets.

Affords complete tannery coverage, concentrated among tanners, chemists and buyers of materials, raw stock and equipment.

Technical articles and newsworthy features invited for publication.

THE LEATHER MANUFACTURER

NEW YORK OFFICE
154 Nassau St.

BOSTON OFFICE
683 Atlantic Ave.

Shoe and Leather REPORTER

TANNERY BUYER

THE TECHNICAL JOURNAL FOR SUPERINTENDENTS, CHEMISTS, TANNERS AND BUYERS

INSIDE TRACK TO BUSINESS!

Why run around "Robin Hood's barn" when there's a quick direct route to customers?

The direct route to tanneries is by way of the TANNERY BUYER, a special monthly section of *Shoe and Leather Reporter*, made especially for and read by important executives, superintendents, chemists, and buyers.

Make your advertising dollars count. Use *Shoe and Leather Reporter's* TANNERY BUYER.

SHOE AND LEATHER REPORTER

Executive Offices: 207 ESSEX STREET, BOSTON 11, MASS.

Offices in: NEW YORK • CHICAGO • MILWAUKEE • CINCINNATI • ST. LOUIS • WASHINGTON • LONDON, ENG.

Salem Oil & Grease Co.

FAT LIQUORS

FEATURING

CONTROLLED PENETRATION

•

SALEM, MASSACHUSETTS

STANDARD HIDE POWDER

A material made to specifications and used internationally for the analysis of vegetable tanning materials

FRANK F. MARSHALL
RIDGWAY · PENNSYLVANIA

Garden State Tanning Inc.
Pine Grove, Pa.

Manufacturers of
Upholstery Leather

New York Office **330 Fifth Avenue**

"The Extension of Knowledge is by the Investigation of Matter".

This space dedicated to
Tanners' Council Research Laboratory
by a Friend

KEPEC FINISHES · KCC CHEMICALS

KEPECO FINNALINE KEPOLAC
EMULLO KEEPA-SHINE FONDO
UNI-LAK
(Reg. U. S. Pat. Office)

KEPEC CHEMICAL CORPORATION
MILWAUKEE 1, WISCONSIN

finest products fastest service

TELEPHONE
BOulevard 8-2030

TRASK EST. 1924

TANNING EXTRACTS
SULFONATED OILS
STUFFING GREASES
LIGNOSULFONATES

ARTHUR C. TRASK CO.
4103 So. LaSalle St., Chicago 9
CABLE: *Actrask* TELETYPE: CG1478

2 to 1

That's the standing of LEATHER AND SHOES in the tanning industry

The latest circulation statement shows that LEATHER AND SHOES has 141% more paid and audited circulation among tanners (audited by the Audit Bureau of Circulations). That's more than double the number of paid subscribers of any other magazine.

But *readership* is even more important. A recent study revealed that at least 3500 top level executives in the tanning industry are reading LEATHER AND SHOES.

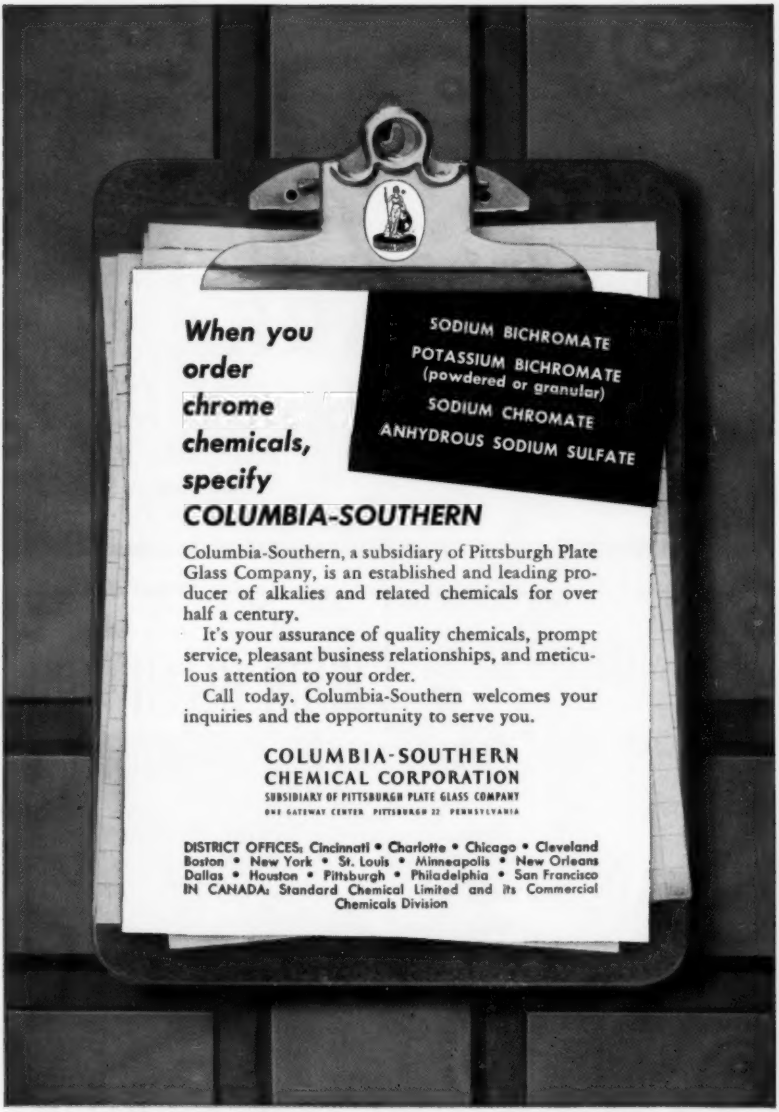
Consider the facts: LEATHER AND SHOES—

. . . does the outstanding job in editorial service.
. . . has twice the paid circulation and considerably more readership.
. . . carries more than double in advertising volume.
. . . does *not* sell advertising on its front cover.
. . . is the industry's most dynamic business paper.

An investment in a subscription to LEATHER AND SHOES will pay dividends in knowledge—an investment in advertising in LEATHER AND SHOES will pay dividends in success. If you want more facts, write us today.

L&S

LEATHER AND SHOES
300 W. ADAMS STREET
CHICAGO 6, ILLINOIS


When you order chrome chemicals, specify
COLUMBIA-SOUTHERN
SODIUM BICHROMATE
POTASSIUM BICHROMATE
(powdered or granular)
SODIUM CHROMATE
ANHYDROUS SODIUM SULFATE
Columbia-Southern, a subsidiary of Pittsburgh Plate Glass Company, is an established and leading producer of alkalies and related chemicals for over half a century.
It's your assurance of quality chemicals, prompt service, pleasant business relationships, and meticulous attention to your order.
Call today. Columbia-Southern welcomes your inquiries and the opportunity to serve you.
COLUMBIA-SOUTHERN
CHEMICAL CORPORATION
SUBSIDIARY OF PITTSBURGH PLATE GLASS COMPANY
ONE GATEWAY CENTER PITTSBURGH 22 PENNSYLVANIA
DISTRICT OFFICES: Cincinnati • Charlotte • Chicago • Cleveland
Boston • New York • St. Louis • Minneapolis • New Orleans
Dallas • Houston • Pittsburgh • Philadelphia • San Francisco
IN CANADA: Standard Chemical Limited and its Commercial Chemicals Division

Finishes
for all types of
Leather

FINE LEATHER FINISHES
NLF

NEWARK
LEATHER FINISH CO.

8 WILHELM ST. HARRISON, N. J.
Telephone: Humboldt 5-3470

HOWES LEATHER CO. INC.
SOLE LEATHER
•
Tanners Cut Sole Division
•
CUT SOLES

BOSTON, MASS.
ST. LOUIS, MO. CHICAGO, ILL.

BONA ALLEN, INC.
Buford, Georgia
TANNERS SINCE 1873
•
Finest English Rein
and Strap Leather
Latigotan Harness Leather
Manufacturers of genuine English
type and full rigged hand tooled
roping saddles.

You meet leather everywhere . . .

in business, traveling, sports, at home. No other material matches its comfortable feel and quiet, good looks.

If you've recently bought a pair of shoes, inspected a fine suitcase, or pounded a baseball glove, you know how leather promises you strength, suppleness and the pride of owning it.

To help impart these qualities to leather, skilled tanners around the world rely on DIAMOND Chromium Chemicals. Working with the leather industry to create ever-lovelier products, DIAMOND research seeks continually to extend the usefulness of these "Chemicals you live by." DIAMOND ALKALI COMPANY, Chromium Chemicals Division, 300 Union Commerce Building, Cleveland 14, Ohio.

DIAMOND ALKALI CHEMICALS

Diamond Chemicals

THIS ADVERTISEMENT reminds the buying public that the advantages of genuine leather cannot be equaled. It's the latest in DIAMOND'S advertising series in support of America's leather industry. Perhaps you saw it—in full color—in TIME, April 4, and NEWSWEEK, April 11.

Here's why SOLVAY Ammonium Bicarbonate does a better job of neutralizing

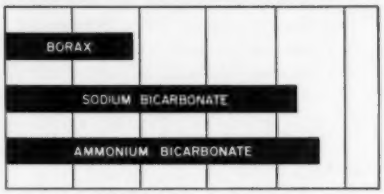
...and gives you these 6 OUTSTANDING ADVANTAGES:

1. Upgrades leathers!
2. Improves grain!
3. More uniform dyeing!
4. More efficient neutralizing!
5. Low pH safeguards against over-neutralizing!
6. Faster penetration!

Superior leathers are obtained with SOLVAY Ammonium Bicarbonate—because it penetrates the leather uniformly throughout the thickness of the hide—the inner part as well as the surface. SOLVAY Ammonium Bicarbonate has a *high neutralizing* value (greater than borax or sodium bicarbonate) with a *low* pH. A 1% solution has a pH of only 7.8!

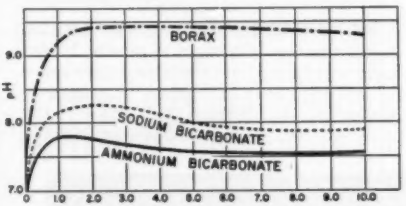
Send for Test Samples of SOLVAY Ammonium Bicarbonate and see how it gives you *better looking leathers—economically* and *efficiently*. Write or phone the SOLVAY office nearest your plant.

1. Higher Neutralizing Power



Pounds of hydrochloric acid neutralized by 1 lb. of alkali

2. Lower pH



Comparative pH of solutions at various concentrations

SOLVAY

Other Solvay Products for Tanners

- CLEANSING SODA XX
- SNOWFLAKE* CRYSTALS

*REG. U.S. PAT. OFF.

Soda Ash • Snowflake® Crystals
Potassium Carbonate
Calcium Chloride
Sodium Bicarbonate
Ammonium Bicarbonate
Cleaning Compounds
Caustic Potash • Sodium Nitrite
Ammonium Chloride • Chlorine
Caustic Soda • Chloroform
Monochlorobenzene
Para-dichlorobenzene
Ortho-dichlorobenzene
Methylene Chloride
Methyl Chloride
Carbon Tetrachloride

SOLVAY PROCESS DIVISION

Allied Chemical

ALLIED CHEMICAL & DYE CORPORATION
61 Broadway, New York 6, N. Y.

BRANCH SALES OFFICES:

Boston • Charlotte • Chicago • Cincinnati • Cleveland • Detroit • Houston
New Orleans • New York • Philadelphia • Pittsburgh • St. Louis • Syracuse

Always Foremost

Armour's QUALITY Leathers USA

SOLE and UPPER LEATHER

●

ARMOUR LEATHER CO.

Chicago Boston New York

THE TANNERS' COUNCIL RESEARCH LABORATORY

at

THE UNIVERSITY OF CINCINNATI

is

THE DEPARTMENT OF BASIC SCIENCE

in

THE GRADUATE SCHOOL OF ARTS AND SCIENCE

The purpose of the laboratory is to conduct scientific research in the fields of Science concerned with Tanning and Leather.

To train Chemists in the technique of research and prepare them for Industry.

This Laboratory serves as the Official Technical Headquarters for the Tanning Industry of the United States.

Your inquiries will be gladly answered.

Address DR. FRED O'FLAHERTY, Director
Tanners' Council Laboratory
University of Cincinnati
Cincinnati 21, Ohio.

VELVETEEN BLACK

A BRIGHT, DEEP BLUE-BLACK NON-INFLAMMABLE FINISH, FOR PLATING OR GLAZING.

USE ON FULL GRAIN OR CORRECTED LEATHERS.

EVEN SPREADING - EXCELLENT COVERAGE
GOOD TIGHTNESS TO WET RUBBING

SAMPLE ON REQUEST

Established 1900
Apex Chemical Co., Inc.
225 West 34th St., New York 1, N. Y.

Manufacturers of a complete line of specialties for the tanning trade

UNION TANNERS SUGAR LIQUID, CHIPPED, BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR
UNION TANNERS SUGAR LIQUID, CHIPPED, BILLETS
NO NG
UN ETS
UN AR
UN ETS
NON-FOAMING UNIFORM CLEAR NON-FOAMING
UNION TANNERS SUGAR LIQUID, CHIPPED, BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR

UNION STARCH & REFINING CO.

Established 1903
General Offices. COLUMBUS, INDIANA

TANIMEX CORP.

350 Fifth Avenue **New York 1, N. Y.**

Prime Importers of

QUEBRACHO EXTRACT

WATTLE EXTRACT H. E. C. BRAND

CHESTNUT EXTRACT LION'S HEAD BRAND

All available in Solid, Pulverized and Spray Dried form.

Raw Tanning Materials of all descriptions.

LEATHER and TANNING MATERIALS

CONSULTING • TESTING • RESEARCH • DEVELOPMENT
for the
TANNING AND ALLIED INDUSTRIES

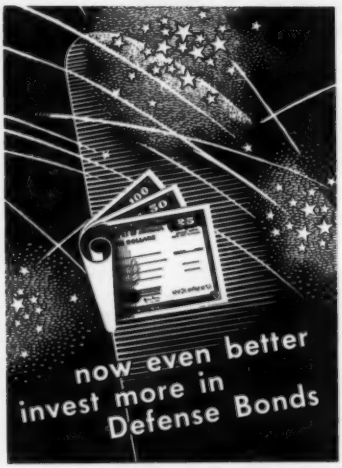
Specialists: Sampling and Testing of Tanning Materials

UNITED STATES TESTING COMPANY

INCORPORATED

1950 Park Avenue, Hoboken, N. J.

LEATHER
& TANNING MATERIALS
TESTING & RESEARCH
Sampling in all U.S. Ports
PENNIMAN & BROWNE, INC.
CHEMISTS - ENGINEERS - INSPECTORS
341 St. Paul Pl.. Balto. 2, Md. MUlberry 5-5811



**RESEARCH
PAYS DIVIDENDS**

when Properly Applied.

**THE TANNER'S COUNCIL
RESEARCH LABORATORY**
University of Cincinnati

**two
good steps . .**

. . . essential to the production of fine leathers are: first, selection of good hides and skins and, second, selection of quality tanning materials.

For years, tanners have selected Clinton corn sugars and Clinton corn syrups as proven materials to use in the chrome tanning process. Clinton Lactic Acid, available in concentrations of 44% or higher, is used as an outstanding deliming and finishing agent.

We know you've already taken the first wise step — selection of good hides. Why not follow up with the second . . . if you haven't already done so? Always choose Clinton for your tanners' sugars, syrups and lactic acid requirements.

Quality products
FROM THE WORLD'S CORN CENTER
CLINTON
CLINTON FOODS INC.
Corn Processing Division
CLINTON, IOWA

INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY, Leather Chemicals Department XI
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXXVIII
ARKANSAS COMPANY, INC. VII
ARMOUR LEATHER CO. XXXVII
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XVI
BARIUM REDUCTION CORPORATION XXV
BARKEY IMPORTING CO., INC. ..... VI—XVIII
BONA ALLEN, INC. XXXIV
BORNE, SCRYMSER COMPANY IX
BUCKMAN LABORATORIES, INC. XII
CHEMTAN COMPANY XXI
CLINTON FOODS XL
COLUMBIA-SOUTHERN CHEMICAL CORP. XXXIII
DIAMOND ALKALI CO. XXXV
EISENDRATH TANNING CO. XXVII
FRANK F. MARSHALL XXXI
GARDEN STATE TANNING INC. XXXI
HOOKER ELECTROCHEMICAL CO. XIX
HOWES LEATHER CO., INC. XXXIV
INTERNATIONAL PRODUCTS CORP. XVII
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES XXXII
LEATHER MANUFACTURER, THE XXIX
L. H. LINCOLN & SON, INC. X
MARDEN WILD CORPORATION XXVI
MEAD CORPORATION, THE V
NEWARK LEATHER FINISH CO. XXXIV
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXVII
OLSON SALES AGENCY, THE ..... Inside Front Cover
PACIFIC COAST BORAX CO. XXVIII
PENNIMAN & BROWNE, INC. XL
PRESTO COLOR CO. XXVIII
REILLY-WHITEMAN-WALTON CO. XXIX
RIVER PLATE CORPORATION, THE XIV
ROBESON PROCESS CO. II
ROHM & HAAS IV
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXVI
SHOE & LEATHER REPORTER XXX
SOCONY MOBIL OIL CO., INC. I
SOLVAY PROCESS DIVISON, ALLIED CHEMICAL & DYE CORP. XXXVI
SOUTH AFRICAN WATTLE EXTRACT MFRS. ASSO. XV
SUN OIL COMPANY XXVI
TANEXCO, INC. ..... XLII —Inside Back Cover
TANIMEX CORPORATION XXXIX
TANNERS' COUNCIL RESEARCH LABORATORY ..... XXXI—XXXVII—XL
TEAS EXTRACT CO. III
UNION STARCH & REFINING CO. XXXVIII
UNITED STATES RUBBER COMPANY XIII
UNITED STATES TESTING COMPANY XXXIX
WALLERSTEIN COMPANY, INC. XXIV
WARNER CO. XXVII
WHITTEMORE-WRIGHT CO. XXVIII
WOLF, JACQUES & CO. VIII
YOUNG CO., J. S. XX

ITALIAN

CHESTNUT EXTRACT

Solid — Powder — Spray Dried

also

MELLOWED CHESTNUT

Highly Soluble — Weight Giving — Good Color

MADE FROM LIVE WOOD

TYPICAL A.L.C.A. ANALYSIS

	Solid	Mellowed Powder	Spray Dried
TANNIN	61.72	65.95	73.5
NON-TANNIN	21.65	26.67	19.1
INSOLUBLES	.65	.67	.7
WATER	15.98	6.71	6.7

STAINLESS SUMAC CRYSTALS

CIPEC

HIGHEST QUALITY—MADE UNDER THE SUPERVISION OF THE WORLD'S LEADING EXTRACT CHEMISTS

SOLE AGENTS

TANEXCO, INC.

549 W. Washington Blvd. Chicago, Illinois

MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

	Ordinary	Clarified
TANNIN	61.55	64.34
NON-TANNIN	16.03	17.14
INSOLUBLES	1.70	0.72
WATER	20.72	17.80

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

For further information address:

TANEXCO, INC.

549 WEST WASHINGTON BLVD., CHICAGO 6, ILLINOIS

SOLE AGENTS
U. S. A.

DERMABATE
COMPOUNDS
LIQUID EXTRACTS

HEMLOCK
OAK
MANGROVE
WATTLE
STAINLESS SUMAC
ORDINARY SUMAC
QUEBRACHO
SPECIAL DIPPING EXTRACTS
RAPID TAN "G"

★

AMERICAN EXTRACT CO.

Manufacturers of the Largest
Variety of Vegetable Tanning Extracts
Established 1887
PORT ALLEGANY, PA.

CANADIAN REPRESENTATIVES:
McArthur Chemical Co., Ltd., 20 St. Paul St., West, Montreal: 73 King St., West Toronto
ENGLISH REPRESENTATIVES:
Roy Wilson, Dickson, Ltd., 7-8 Railway Approach, London, S. E. 1